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ANALYTICAL PROCEDURES FOR CHARACTERIZING UNREGULATED POLLUTANT EMISSIONS FROM MOTOR VEHICLES

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FOREWARD

The Clean Air Act, in the August 1977 amendments, calls for assurance that no emission control device, system, or element of design used in a new motor vehicle or new motor vehicle engine cause or contribute to an unreasonable risk to public health, welfare, or safety. This mandate implies the measurement of a variety of presently non-regulated compounds in the exhaust and/or evaporative emissions from such vehicle. The Environmental Protection Agency, in Advisory Circular 76, and in other documents currently in review, calls for measurement of many potentially hazardous compounds.

The Environmental Sciences Research Laboratory in EPA's Office of Research and Development is currently sponsoring a contractual effort at Southwest Research Institute, San Antonio, Texas wherein the emission rates of several non-regulated pollutants from three-way catalyst equipped motor vehicles are being examined. This document describes in detail the analytical procedures being used in this study. These procedures are not necessarily the best or only means of determining the emission rates of the compounds of interest. They represent an assessment of the optimum procedures available at the time of the contract.

Comment is herewith being solicited from any laboratory attempting to apply the defined procedures. If difficulties are experienced, improvements defined, or new procedures developed, please communicate same to the EPA Project Officer and at appropriate time intervals a document will be issued transmitting this information to all holders of the base document.

Ronald L. Bradow

Dr. Ronald L. Bradow, Chief
Mobile Source Emissions Research Branch
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ABSTRACT

Analytical procedures are described that may be used to assess motor vehicle emission rates of several unregulated pollutants including aldehydes, organic amines, sulfur dioxide, nitrous oxide, several individual hydrocarbons including benzene, hydrogen sulfide, total cyanide, organic sulfides, nickel carbonyl, ammonia, sulfate, and N-nitrosodimethylamine (sampling conditions only). A series of validation experiments involving motor vehicle exhaust with injects of known quantities of the compounds of interest and the Constant Volume Sampling system commonly used in emissions certification are described for several of the analytical procedures. The Clean Air Act as amended August 1977 requires in section 202(a) 4 that unregulated pollutants emitted from motor vehicles be measured to assure that no unreasonable risk to public health and welfare exists.

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The project, "Characterization of Emissions from Motor Vehicles Designed for Low NO_x Emissions", for which this report is a part was initiated by the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. The scientific and engineering effort on which this report is based was accomplished by the Department of Emissions Research, Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas, under EPA Contract Number 68-03-2497. This report, designated as Interim Report II, encompasses the effort to accomplish Task II of this project, Qualification of Methodology. Task II of this project began September 1977 and was completed November 1978. The EPA Project Officer during this period was Frank Black. The project was initially under the supervision of Sherrill F. Martin, Project Leader, and Harry Dietzmann, Senior Research Chemist. Lawrence R. Smith, Senior Research Scientist, and Harry Dietzmann directed the project beginning August 1978. This project was identified within Southwest Research Institute as Project 11-4840-001.

SECTION 1

INTRODUCTION

The objective of this project is to select, qualify, and then utilize suitable measurement instrumentation and techniques for the characterization of regulated and a variety of currently non-regulated exhaust emissions from gasoline automobiles using various catalytic methods to achieve low oxides of nitrogen. Task I of this project includes a detailed literature search to determine candidate analytical methods for each of the following compounds or group of compounds.

Nitrous Oxide
Hydrogen Cyanide
Ammonia
Cyanogen
Organic Amines
N-nitrosodimethylamine
Hydrogen Sulfide
Sulfuric Acid
Sulfur Dioxide
Carbonyl Sulfide
Organic Sulfides
Nickel Carbonyl

The analytical methods chosen for Task II were selected by the Project Officer. Task II includes the validation and qualification of the analytical methods selected in Task I. Task III involves the use of the selected analytical methods to measure exhaust emissions from gasoline automobiles which use catalytic methods to achieve low oxides of nitrogen.

This report is a summary of the results of Task II in which the selected analytical methods of Task I are validated. A review of the literature search of Task I, procedural development work, validation experiments, and qualification experiments for ten analytical procedures are discussed. These procedures include: aldehyde and ketone procedure (Section 2), organic amine procedure (Section 3), sulfur dioxide procedure (Section 4), nitrous oxide procedure (Section 5), individual hydrocarbon procedure (Section 6), hydrogen sulfide procedure (Section 7), total cyanide procedure (Section 8), organic sulfide procedure (Section 9), nickel carbonyl procedure (Section 10), and ammonia procedure (Section 11). Interim Report I, a finalized copy of the analytical procedures discussed in Section 2-11, the BCA sulfate procedure, and sampling conditions for DMNA are included as an appendix.

SECTION 2

ALDEHYDE AND KETONE PROCEDURE

LITERATURE SEARCH

The individual aldehydes and ketones that are included in this analysis are: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, isobutyraldehyde, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde. Acetone, acrolein, and propionaldehyde are not resolved from each other under normal gas chromatographic operating conditions and all three are reported together as acetone. The common names, the International Union of Chemists approved names, the chemical formulas, the molecular weights, the melting points, the boiling points, the densities, the molecular weights of the 2,4 dinitrophenylhydrazone derivative, and the melting points of the 2,4 dinitrophenylhydrazone derivative are presented in Table 1. The aldehydes and ketones have a characteristicly pungent odor, are flammable, are photochemically reactive, can cause respiratory problems, and are severe eye irritants. The 1976 American Conference of Government Industrial Hygienists has recommended threshold limit values for several of the aldehydes and ketones (1). These values range from 0.1 ppm for acrolein to 1000 ppm for acetone. Other values listed were 2 ppm for formaldehyde and crotonaldehyde, 100 ppm for acetaldehyde and 200 ppm for methlethylketone.

PROCEDURAL DEVELOPMENT

A procedure, which is already in use at Southwest Research Institute, developed by the Mobile Source Emissions Research Branch of the ESRL-EPA at Research Triangle Park, North Carolina, was selected for the analysis of the aldehydes and ketones (2). This procedure involves bubbling exhaust through glass impingers containing 2,4 dinitrophenylhydrazine (DNPH) in dilute hydrochloric acid. The exhaust sample is collected continuously during a test cycle. The aldehydes and ketones (also known as carbonyl compounds) react with the DNPH to form their respective phenylhydrazone derivatives. These derivatives are either insoluble or only slightly soluble in the DNPH/HCl solution and are removed by filtration followed by pentane extractions. The filtered precipitate and the pentane extracts are combined, and the pentane is evaporated in a vacuum oven. The remaining dried extract contains the phenylhydrazone derivatives. The extract is dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. A portion of this extract is injected into a gas chromatograph and analyzed using a flame ionization detector. A copy of this procedure as used by the Department of Emissions Research at Southwest Research Institute will be included as an attachment to this report.

TABLE 1. PHYSICAL PROPERTIES OF THE ALDEHYDES AND KETONES (3,4)

Aldehyde or Ketone	ICU Name	Chemical Formula	Molecular Weight	Melting Point	Boiling Point	Density	Molecular Weight DNPH Derivative	Melting Point Der.
Formaldehyde	Methanal	CH_2O	30.03	- 92	- 21	0.815	210.15	167
Acetaldehyde	Ethanal	CH_3CHO	44.05	-121	21	0.783	224.19	168
Acetone	2-Propanone	CH_3COCH_3	58.08	- 95	56	0.790	238.21	128
Propionaldehyde	Propanal	CH_3CH_2CHO	58.08	- 81	49	0.806	238.21	156
Acrolein	Propenal	$CH_2:CHCHO$	56.07	- 87	53	0.841	236.20	165
Isobutyraldehyde	2-Methylpropanal	$CH_3CH(CH_3)CHO$	72.11	- 65	63	0.794	252.23	182
Methylethylketone	2-Butanone	$CH_3COCH_2CH_3$	72.11	- 84	80	0.805	252.23	---
Crotonaldehyde	trans2-Butenal	$CH_3CH:CHCHO$	70.09	- 74	105	0.850	250.21	190
Hexanaldehyde	Hexanal	$CH_3(CH_2)_4CHO$	100.16	- 56	128	0.814	279.28	104
Benzaldehyde	Benzenecarbonal	C_6H_5CHO	106.13	- 26	178	1.042	286.25	237

VALIDATION EXPERIMENTS

Several experiments were carried out to determine the validity of the DNPH procedure for the analysis of the aldehydes and ketones. These experiments included checks for: GC injection variability, linearity of detector response, sample stability in the DNPH absorbing solution and in toluene, trapping efficiency of the DNPH/HCl solution, interferences, and extraction plus injection repeatability.

The finalized sampling conditions used to collect the aldehydes and ketones are listed below as is a discussion on their selection. Two glass impingers in series, each containing 40 mℓ of 2 N HCl/2-4 dinitrophenylhydrazine, are used to collect the aldehydes and ketones. The two impingers together trap 98+ percent of the carbonyl compounds. This collection efficiency was determined by bubbling known amounts of the aldehydes and ketones through a series of impingers and analyzing each impinger separately. No advantage was found in using more than two impingers. There was no observed difference in analyzing the contents of the two impingers separately or combined. Since the analysis of the two impingers combined is less manpower intensive, the two impingers are analyzed together. During sampling, the two impingers are kept in a 0°C ice bath. The ice bath offers no significant advantage in collection efficiency over room temperature, but does provide a stable sampling temperature during the test. The 0°C temperature also lowers the vapor pressure of the aqueous absorbing solution and thus prevents loss of any significant amount of water from the absorbing solution during sampling. The sample flow rate through the impingers is maintained at 4 liters a minute. This flow provides the largest amount of sample to flow through the absorbing reagent without loss in absorbing efficiency or the physical loss of any absorbing reagent. A teflon sample line connecting the CVS to the impingers is heated to 77°C in order to prevent water from condensing in the sample line. Some of the aldehydes and ketones are water soluble, and the condensation of water in the sample line could cause a significant loss of sample in the sample line.

The HCl/DNPH absorbing reagent has been found to be stable over several days; however, to prevent the possibility of contamination or the inadvertant use of "old " absorbing reagent, the solution is prepared daily as needed.

The samples have been found to be stable for at least two days in the absorbing reagent. However, to prevent the possibility of contamination of the samples by their standing in the lab for prolonged periods, the samples are extracted, dried, and dissolved in toluene all in the same day. Once the sample is dissolved in toluene it is stable for relatively long periods of time. Samples run and re-run over a period of two weeks showed no significant change in concentrations.

To determine the GC injection repeatability for the procedure over a wide range of concentrations, four standards containing 1.6, 0.2, 0.02 and 0.002 mg of each aldehyde and ketone DNPH derivative per mℓ of toluene were prepared. These are the concentration ranges expected when sampling dilute exhaust. Each standard was injected into the GC five consecutive times.

The concentration determined by the procedure for each of the derivatives was averaged over the 5 runs, and a standard deviation as well as a percent standard deviation was calculated. The results of these injection repeatability experiments are presented in Table 2. The injection repeatability is good for the 1.6 mg derivative/mℓ toluene standard (percent deviation ranges from 1.1 percent for formaldehyde to 9.6 percent for benzaldehyde) and the 0.2 mg derivative/mℓ toluene standard (percent deviation ranges from 0.5 percent for acetaldehyde to 5.9 percent for benzaldehyde). At the two lower concentrations the standard deviation in the injection repeatability was found to be much larger. The 0.02 mg derivative/mℓ toluene standard gave percent deviations ranging from 3.7 percent for acetone to 32 percent for benzaldehyde. The 0.002 mg derivative/mℓ toluene standard gave percent deviations which ranged from 10 percent for formaldehyde to 110 percent for benzaldehyde. It appears from the data that the injection repeatability is good at higher derivative concentrations, but much more erratic at very low concentrations.

To determine the linearity of the detector for the concentration ranges of interest for each of the derivatives, seven standard solutions were prepared which contained 8.0, 4.0, 1.6, 0.8, 0.2, 0.02, and 0.002 mg of each derivative/mℓ toluene. These standards were made by weighing out required amounts of each derivative and dissolving them in the appropriate amount of toluene to give the required concentrations. The solution containing 0.2 mg of each derivative/mℓ toluene was used as the standard and the other six solutions were compared to this standard. Figures 1-8 show plots of the procedure determined concentration vs the actual concentration on a log-log scale. Acetone, methylethylketone, and crotonaldehyde give linear plots throughout the region of interest. Formaldehyde, acetaldehyde, isobutyraldehyde and hexanaldehyde give linear plots except at the lower concentrations (<0.02 mg der/mℓ toluene). Benzaldehyde gives a plot which is not linear above 2.0 mg/mℓ toluene. The benzaldehyde-DNPH derivative is not soluble in toluene at concentrations greater than 2.0 mg/mℓ. This fact should be taken into account if high concentrations of benzaldehyde are expected (>5 ppm for a 23 minute sampling period at 4 ℓ/min).

An experiment was carried out to determine the extraction repeatability for the DNPH procedure at low concentrations of DNPH-aldehyde derivatives. One liter of DNPH absorbing solution containing small amounts of pure formaldehyde, acetaldehyde, acetone, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde DNPH derivatives was prepared. Seven extractions (80 mℓ for each extraction) were carried out over a period of two weeks. The results from the extractions are presented in Table 3. These results were determined in units of mg DNPH derivative/mℓ of toluene. The values for each of the seven extractions, the average, and the standard deviation are listed for each of the aldehydes and ketones. Multiple injections were also carried out on each sample over the two week period. The values obtained generally did not vary more than 0.002 mg derivative/mℓ toluene (except for two DNPH-acetone values). This finding indicates, for several of the compounds, that a large part of the variation in values was due to the extraction process and not the lack of injection repeatability.

The results of these experiments indicate that the variability in the

TABLE 2. INJECTION REPEATABILITY

DNPH Aldehyde or Ketone Derivative	1.6 mg derivative/ml			0.2 mg derivative/ml			0.020 mg derivative/ml			0.002 mg derivative/ml		
	Avg. for 5 Inject.	Standard Std. Dev.	% Dev.	Avg. for 5 Inject.	Standard Std. Dev.	% Dev.	Avg. for 5 Inject.	Standard Std. Dev.	% Dev.	Avg. for 5 Inject.	Standard Std. Dev.	% Dev.
Formaldehyde	1.567	0.018	1.1	0.188	0.007	3.7	0.022	0.002	9.1	0.007	0.0007	10
Acetaldehyde	1.727	0.022	1.3	0.201	0.001	0.5	0.024	0.002	8.3	-----	------	--
Acetone	1.617	0.018	1.1	0.210	0.002	0.9	0.027	0.001	3.7	0.002	0.0007	35
Isobutyraldehyde	1.561	0.017	1.1	0.208	0.002	1.0	0.020	0.001	5.6	-----	------	--
Methylethylketone	1.575	0.029	1.8	0.206	0.003	1.5	0.024	0.001	4.2	0.003	0.0007	23
Crotonaldehyde	1.781	0.053	3.0	0.206	0.003	1.5	0.015	0.001	6.7	0.002	0.0007	35
Hexanaldehyde	1.682	0.105	6.2	0.204	0.003	1.5	0.015	0.001	6.7	0.001	0.0007	70
Benzaldehyde	1.710	0.165	9.6	0.222	0.013	5.9	0.025	0.008	32	0.001	0.0011	110

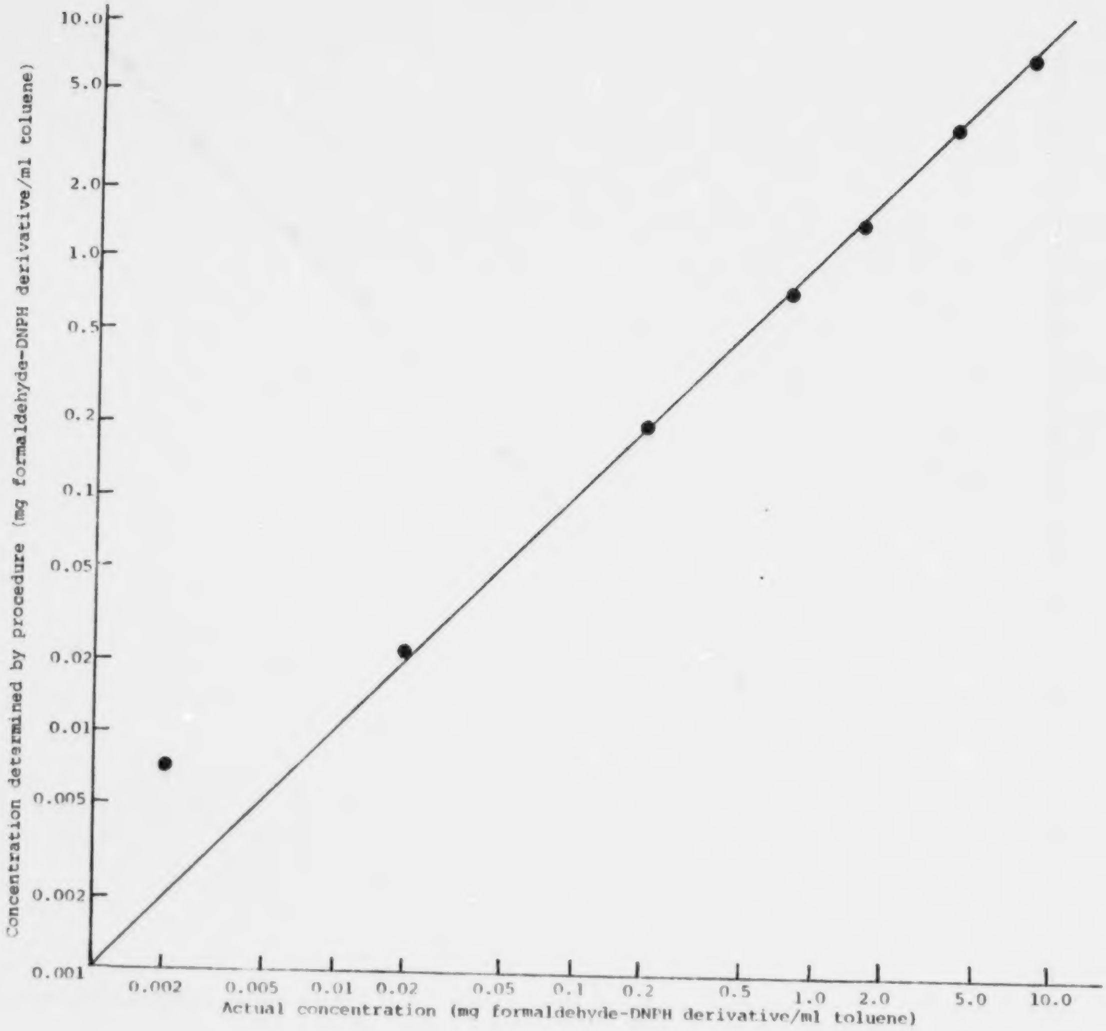

Figure 1. Plot of the formaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

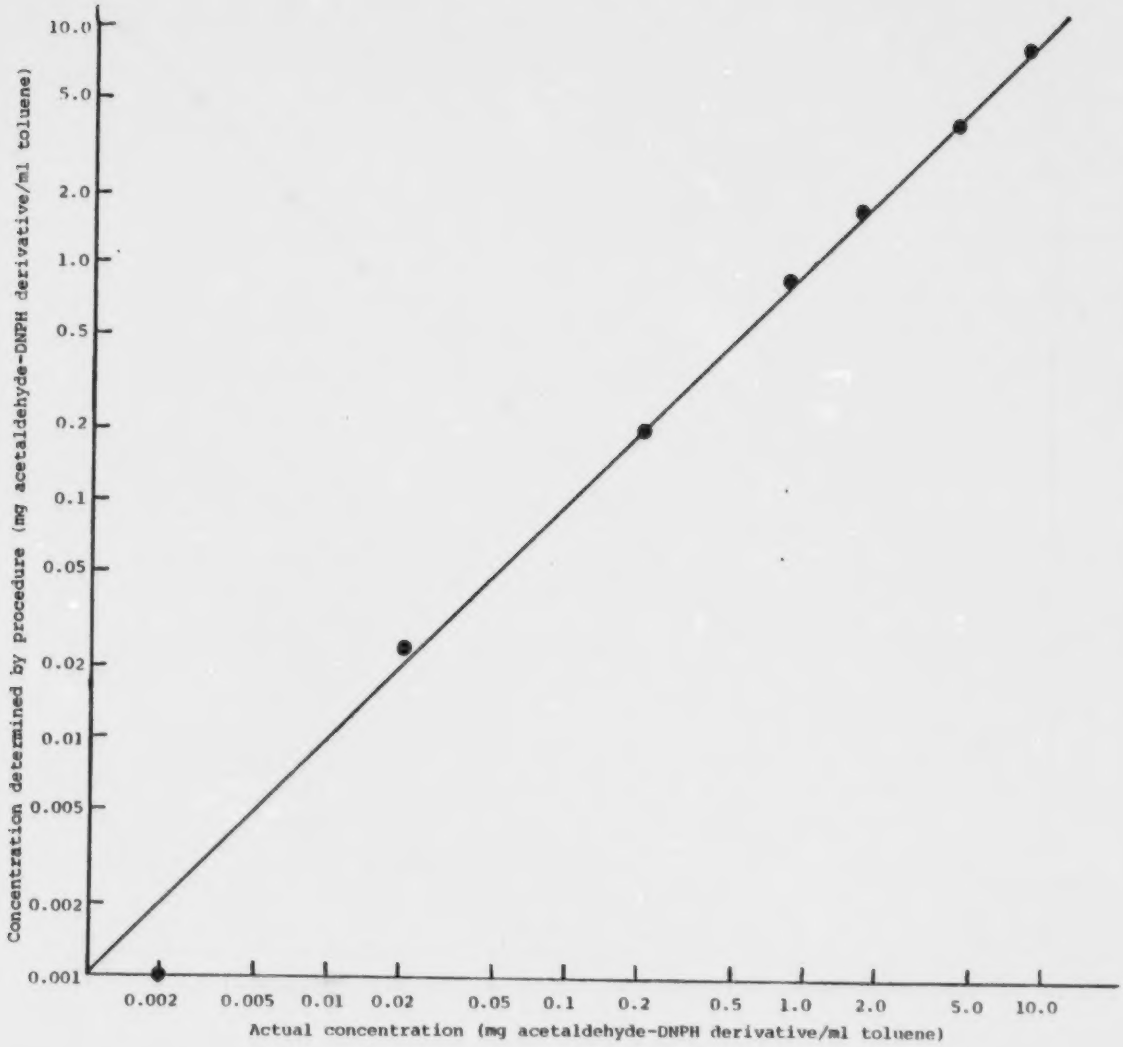

Figure 2. Plot of the acetaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

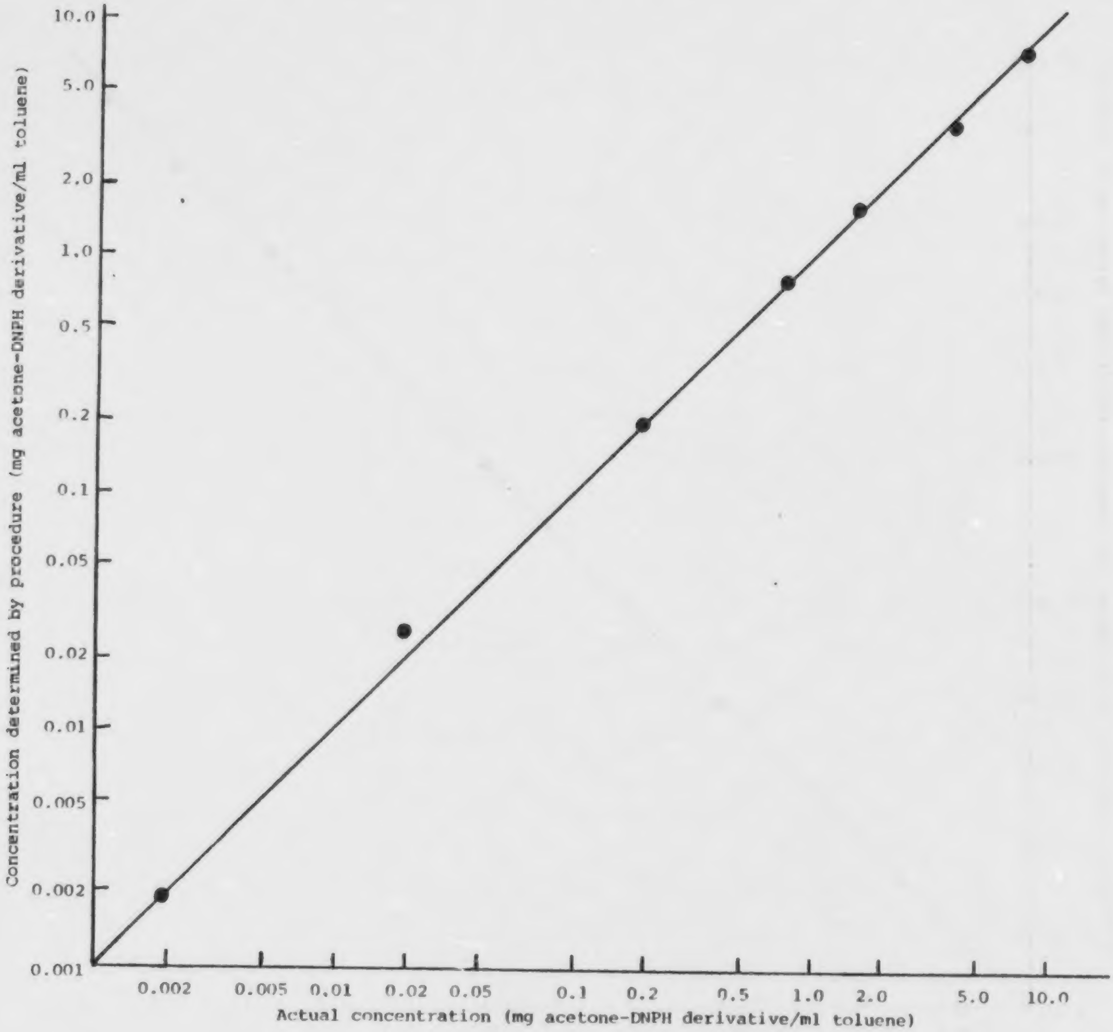

Figure 3. Plot of the acetone-DNPH derivative concentration determined by procedure vs actual concentration.

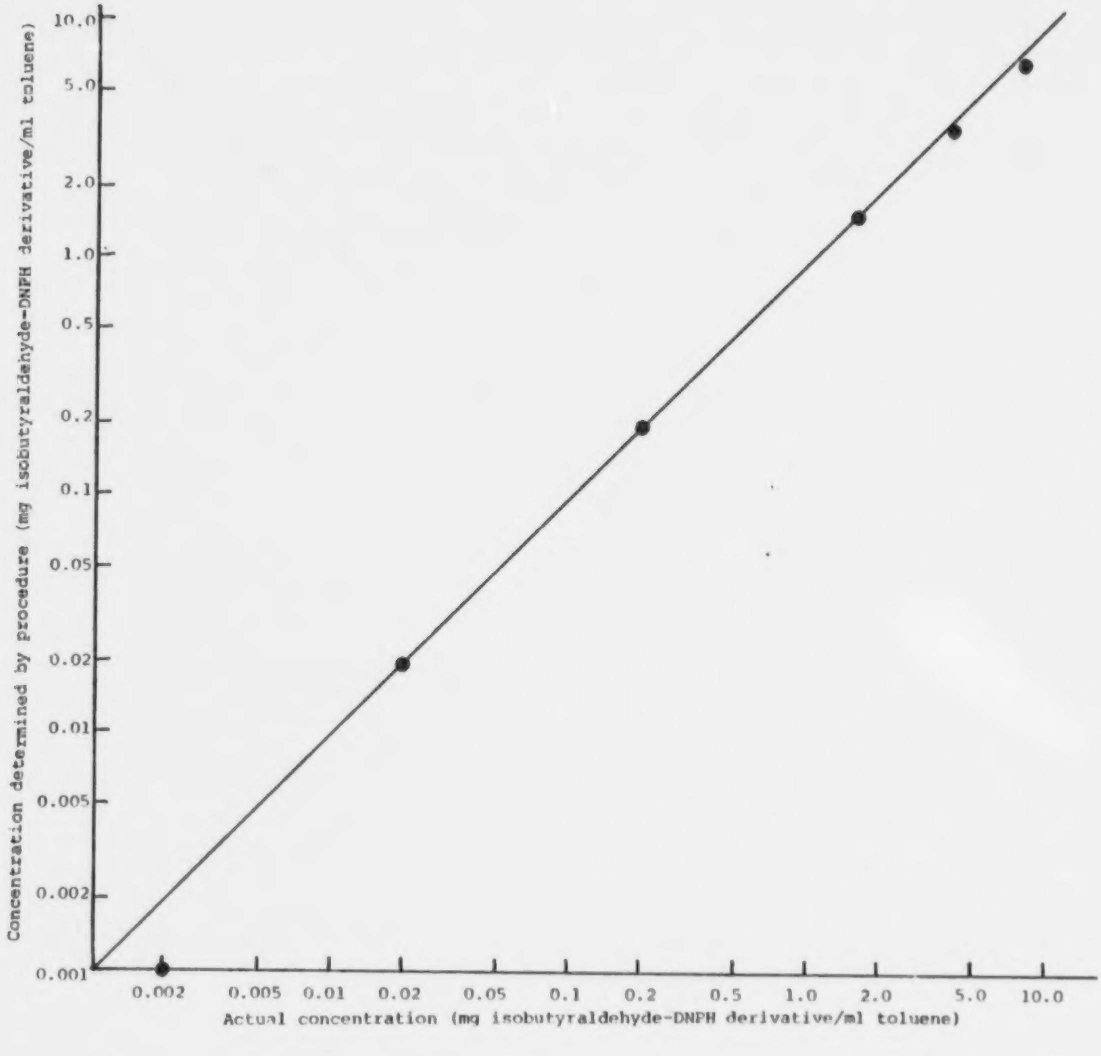

Figure 4. Plot of the isobutyraldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

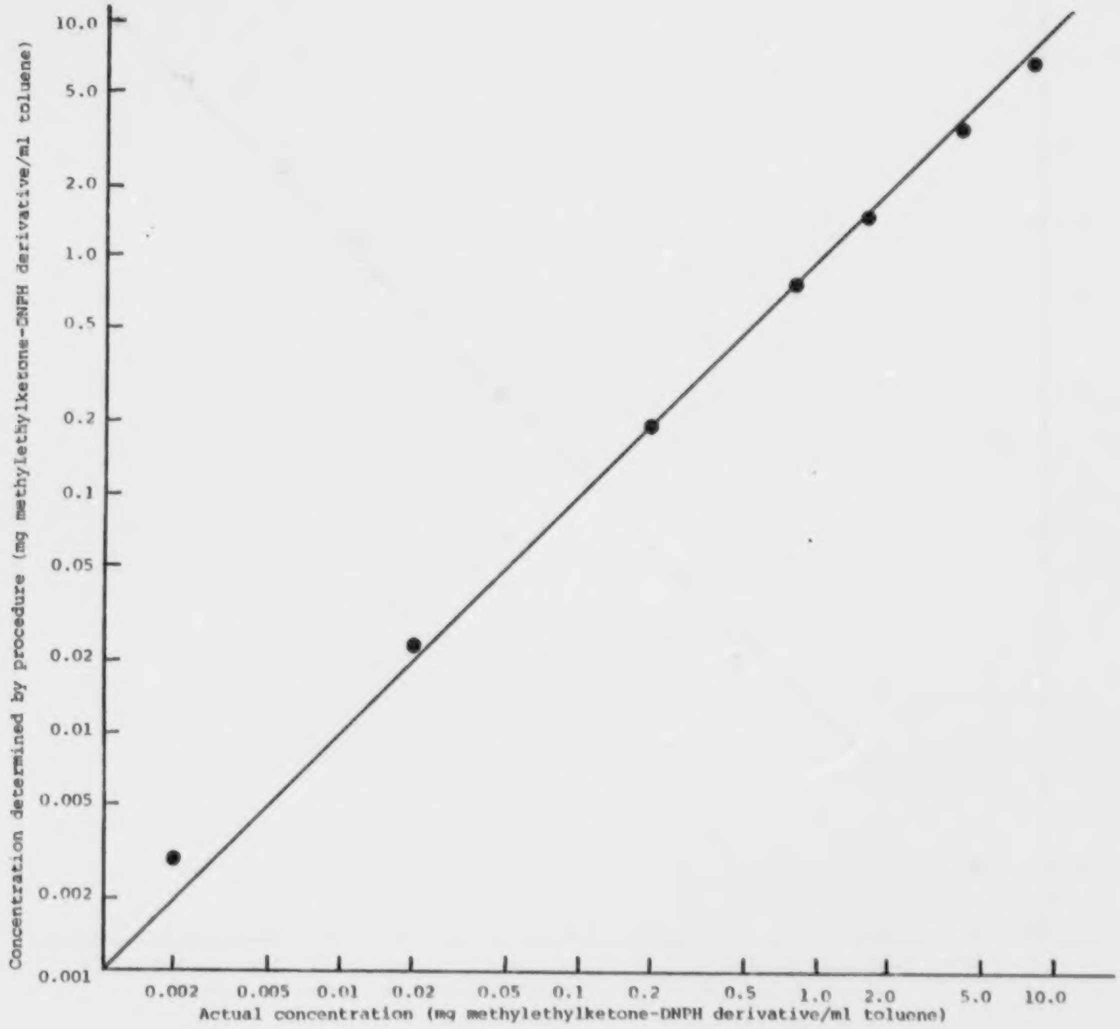

Figure 5. Plot of the methylethylketone-DNPH derivative concentration determined by procedure vs actual concentration.

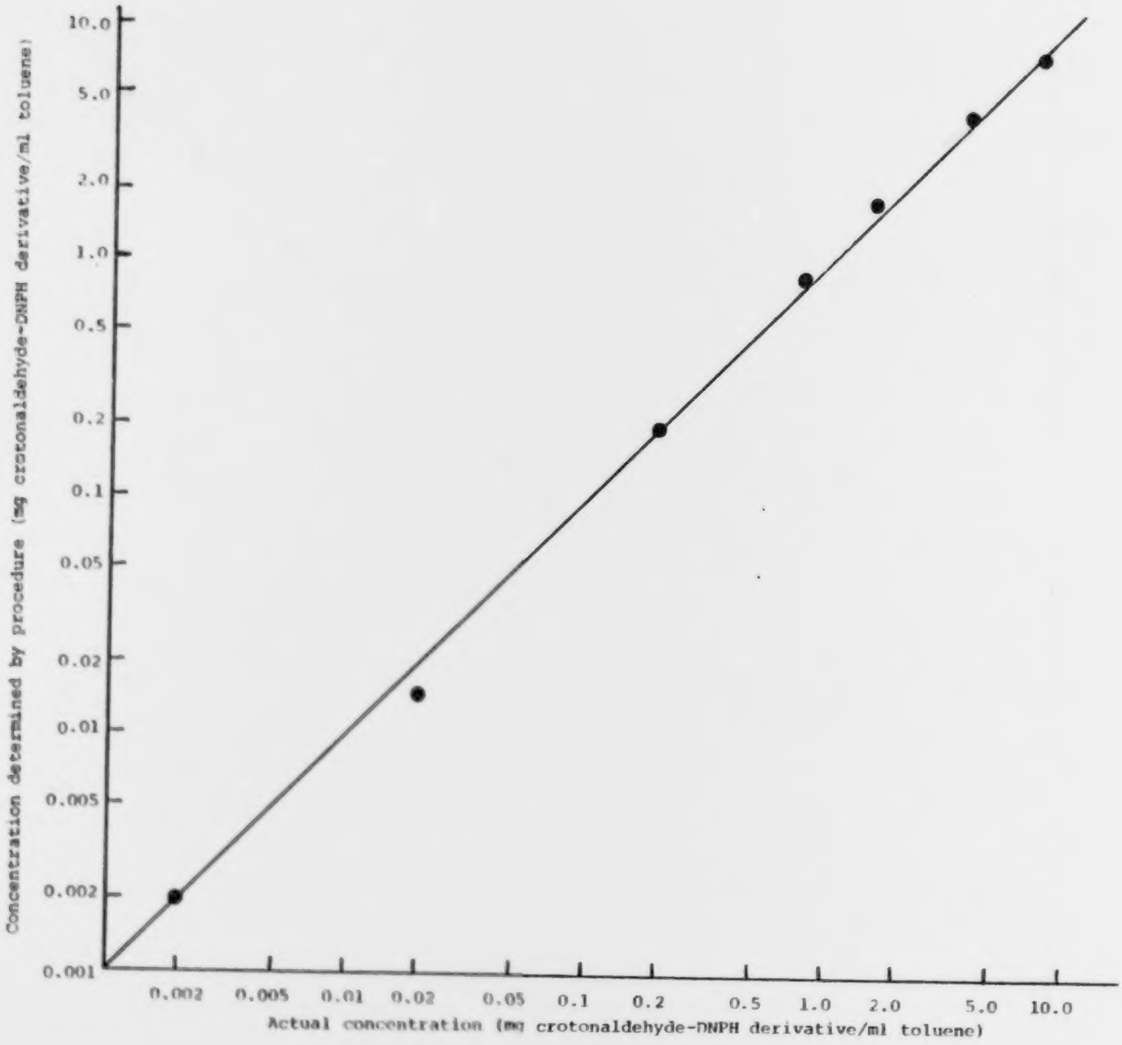

Figure 6. Plot of the crotonaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

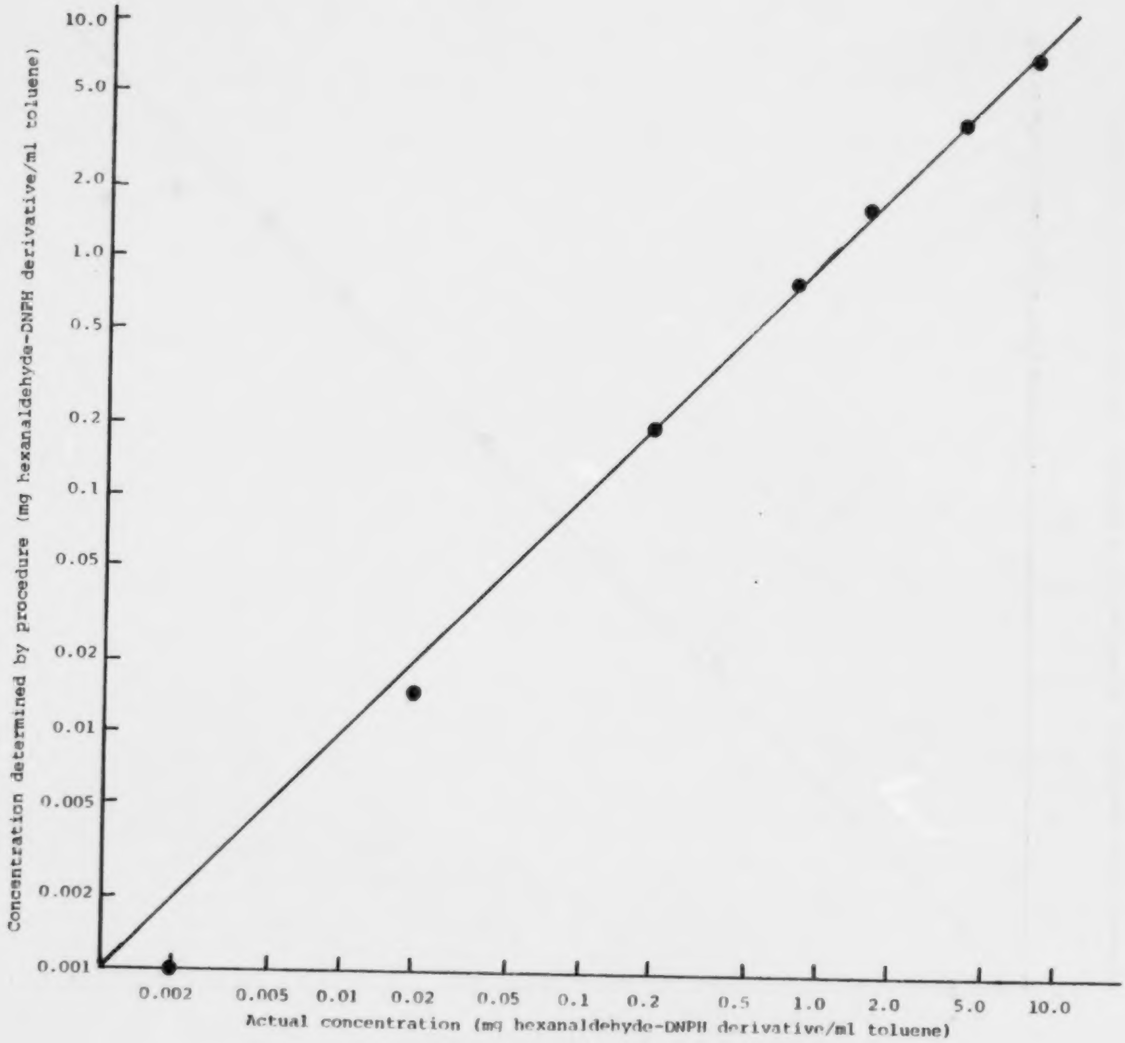

Figure 7. Plot of the hexanaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

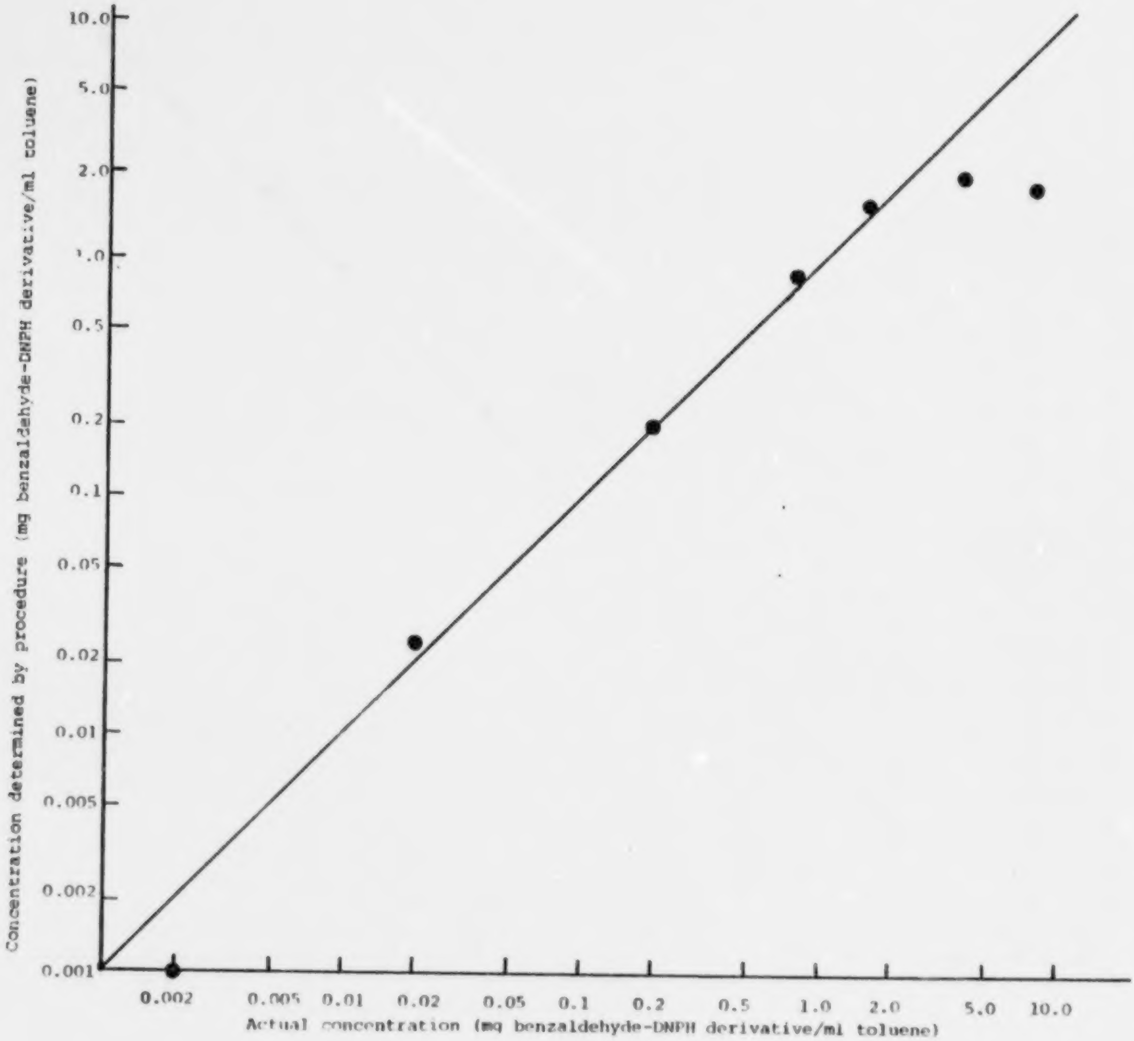

Figure 8. Plot of benzaldehyde-DNPH derivative concentration determined by procedure vs actual concentration.

TABLE 3. MULTIPLE EXTRACTIONS OF DNPH SOLUTIONS
(All Units are mg DNPH derivative/mℓ of Toluene)

Extraction	Form-aldehyde	Acet-aldehyde	Acetone	MEK	Cronton-aldehyde	Hexan-aldehyde	Benz-aldehyde
First	0.018	0.011	0.005	0.000	0.003	0.001	0.014
Second	0.023	0.037	0.015	0.003	0.004	0.002	0.027
Third	0.020	0.032	0.015	0.000	0.003	0.001	0.044
Fourth	0.009	0.013	0.005	0.000	0.002	0.000	0.000
Fifth	0.014	0.019	0.007	0.000	0.003	0.002	0.014
Sixth	0.020	0.031	0.014	0.004	0.005	0.002	0.004
Seventh	0.014	0.027	0.043	0.014	0.004	0.000	0.007
Average	0.017	0.024	0.015	0.003	0.003	0.001	0.016
Standard Deviation	±0.005	±0.010	±0.013	±0.005	±0.001	±0.001	±0.015

extraction process for concentrations of DNPH aldehyde and DNPH ketone derivatives below 0.025 mg DNPH derivative/mℓ toluene can be very significant (i.e., 94 percent for benzaldehyde at 0.016 mg/mℓ). This variability needs to be taken into account when evaluating data obtained using this procedure. At higher DNPH derivative concentrations (0.2-2.0 mg derivative per mℓ toluene) the overall test variability (trapping, extraction and injection) is approximately 10 percent. This value was obtained from the standard deviation of tunnel recovery and trapping efficiency experiments.

The DNPH analysis for the aldehydes and ketones has given abnormally high concentrations of crotonaldehyde and benzaldehyde in isolated occasions. A gas chromatography-mass spectroscopy study was carried out on three samples obtained from EPA contract 68-03-2499. The three samples either contained abnormally high concentrations of crotonaldehyde DNPH derivative or benzaldehyde-DNPH deriavtive or both. The results from this study revealed that neither crotonaldehyde nor benzaldehyde was present in the samples. Further gas chromatography-mass spectroscopy studies were carried out on two ot the samples to determine what compounds were present. In both samples, the crotonaldehyde peaks were due to a phthalate, and the benzaldehyde peaks could not be identified. This study revealed that the samples contained several other phthalates as well as di-2-ethylhexyladipate (a fuel stabilizer). Many phthalate esters (e.g., dioctyl, dibutyl, dimethyl, etc.,) are found in lubricants and plastics. It is possible that the phthalate peaks found in the above samples were due to contamination in the extraction process (e.g., from a pipette bulb, etc.). In subsequent testing, extreme care will be taken to assure the samples do not come into contact with plastics and other materials which could cause contamination. It is also possible that some of the phthalates which are found in small quantities in the samples are from the exhaust (originating from lubricants) and are possible interferences in the procedure. Also, the di-2-ethylhexyladipate appears to produce a minor interference.

QUALIFICATION EXPERIMENTS

Qualification Experiments were carried out using a 1972 Plymouth Fury with a 360V-8 engine (no catalyst). Hot FTP (23 minute test) driving cycles were followed to generate exhaust for the vehicle baseline emissions and for the tunnel injection + vehicle experiments. An aluminum cylinder containing 1350 ppm propionaldehyde in balance nitrogen was used as the source for aldehydes in the experiments. The cylinder was named using the aldehyde-DNPH procedure. The flow of propionaldehyde into the tunnel was regulated to give a concentration of 1-2 ppm propionaldehyde in the dilution tunnel. Injections of propionaldehyde into the tunnel without exhaust gave recoveries that ranged from 85 percent to 121 percent with an average of 103 percent (Table 1). The recovery of propionaldehyde with real vehicle exhaust ranged from 78 percent to 115 percent with an average of 100 percent (Table 4). The injections with the vehicle were corrected for the vehicle baseline emission of propionaldehyde. If propionaldehyde is representative of the aldehydes, then it appears that there is little or no loss of the aldehydes in the dilution tunnel with or without exhaust present.

TABLE 4. PERCENT RECOVERY OF PROPIONALDEHYDE

Tunnel Only		Tunnel + Vehicle	
Run	Recovery %	Run	Recovery %
1	117	1	90
2	116	2	115
3	85	3	106
4	89	4	106
5	121	5	85
6	89	6	103
Avg	103	7	78
		8	110
		Avg	100

RESULTS AND CONCLUSIONS

The concentration of aldehydes and ketones in dilute exhaust can be determined by (1) trapping the aldehydes and ketones in a DNPH/HCl absorbing solution, (2) removing the resulting derivative from the absorbing solution by filtration and extraction with pentane, (3) evaporating off the pentane (4) dissolving the dried extract in toluene, and (5) analyzing the resulting solution with a gas chromatograph equipped with a flame ionization detector. The aldehydes and ketones are effectively trapped in the absorbing solution at a flow rate of 4 ℓ/min. The procedure has a minimum detection limit of approximately 5 ppb. This carbonyl concentration in the exhaust gives a corresponding concentration of 0.002 mg/mℓ in toluene.

The accuracy of the procedure in the 0.5-20 ppm concentration range for the aldehydes or ketones in dilute exhaust is approximately 10 percent. The accuracy of the procedure in the 0-0.05 ppm range is not as good and values can vary as much as 100 percent. The gas chromatograph system gives a linear response for acetone, methylethylketone, and crotonaldehyde DNPH-derivative concentrations between 0.002 and 8 mg derivative/mℓ toluene and gives a linear response for formaldehyde, acetaldehyde, isobutyraldehyde and hexanaldehyde DNPH derivative concentrations between 0.02 and 3 mg derivative/mℓ toluene. The benzaldehyde-DNPH derivative give a linear response in the 0.02 to 2 mg derivative/mℓ toluene concentration range. The benzaldehyde derivative is not soluble at concentrations greater than 2 mg/mℓ toluene.

Phthalates and di-2-ethylhexyladipate were found by mass spectroscopy to be interferences in the procedure. Many phthalate esters (e.g., dioctyl, dibutyl, dimethyl, etc.) are found in lubricants and plastics, and di-2-ethylhexyladipate is used as a fuel stabilizer. Contamination from phthalates could occur in the extraction process or in sample storage if the sample is allowed to come into contact with plastics, a pipette bulb, a lubricant, etc. It is also possible that some phthalates originate from the exhaust (from lubricants) and are possible interferences in the procedure. The benzaldehyde and crotonaldehyde values can be affected by these interferences. The interfering peak in the region of benzaldehyde is usally broad and the benzaldehyde peak, if present, can be observed on top of this interference. If care it taken, a reliable value can be determined for the benzaldehyde. Any value reported for crotonaldehyde may be artifically high due to possible phthalate contamination. Extreme care must be taken when handling the sample in order to eliminate any possibility of contamination after collecting the sample and before analysis.

Propionaldehyde can be recovered quantitatively from the dilution tunnel with or without exhaust present. If propionaldehyde is representative of the aldehydes and ketones, there is little or no loss of the aldehydes in the dilution tunnel with or without exhaust present.

Overall the DNPH procedure should provide a relatively accurate method for determining the concentration of aldehydes and ketones in dilute exhaust, and its use is recommended for this project.

SECTION 3

ORGANIC AMINE PROCEDURE

LITERATURE SEARCH

The individual amines that are included in this analysis are monomethylamine, dimethylamine, monoethylamine, trimethylamine, diethylamine and triethylamine. The chemical formulas, molecular weights, boiling points, freezing points, and synonyms for these low molecular weight aliphatic amines are presented in Table 5. In general, these amines have a fish-type odor at lower concentrations, but more of an ammoniacal odor at higher levels. The 1968 American Conference of Governmental Industrial Hygientists has recommended a threshold limit value of 10 ppm.

The measurement of individual low molecular weight amines has been conducted using a variety of gas chromatograph techniques. Hoshike (6,7) reported gas chromatographic separation of lower aliphatic amines in the free form and as their Schiff base derivatives. A glass column was employed to provide a separation of 11 amines using temperature programming and a thermal conductivity detector. This work was directed toward achieving a satisfactory separation rather than being concerned with minimum detection limits. Sze (8), et al reported separation of methyl amines, ammonia, and methanol using a mixture of tetrahydorxyethylethlenediamine and tetraethylenepentamine. O'Donnel and Mann (9) used Dowfax 9N9, Carbowax 400, and Carbowax 20M to separate mixtures of aliphatic amines, aromatic amines, and aliphatic amines. This work was performed using synthetic blends on a gas chromatograph with a thermal conductivity detector. McCurdy and Meiser (10) used a gas chromatograph with a flame ionization detector to determine fatty amines in trace quantities. The fatty amines were converted to trifluoracetyl derivatives, providing a sensitivity of 0.05 ppm fatty amine in water.

Smith and Waddington (11) used aromatic polymer beads to separate a wide range of aliphatic amines. Peak tailing was found to exist because of two types of active sites on the polymer: simple acidic sites which can be neutralized by treatment with base, and metal ions which must be deactivated by addition of an involatile complexing agent. Glass columns were used in a gas chromatograph with a flame ionization detector. Synthetic blends ranging from C_1-C_6 were separated and analyzed using this approach. In another study Carbopak B/4 percent Carbowax 20 M/0.8 percent KOH (12) and 28 percent Pennwalt 223/4 percent KOH (13) have been reported to give satisfactory separations of lower aliphatic amines.

Analysis of amines as derivatives has been shown to be a valuable analytical tool to determine trace quantities (14). Thirteen different

TABLE 5. LIST OF INDIVIDUAL ORGANIC AMINES INCLUDED IN THE EMISSIONS CHARACTERIZATION INVENTORY

Name		Carbon No.	Chemical Formula	Molecular Weight	Boiling Point, °C	Freezing Point, °C	Synonyms
Monomethylamine	(5)	1	CH_3NH_2	31.058	- 6.32	- 93.5	Methylamine, aminomethane
Monoethylamine	(5)	2	$C_2H_5NH_2$	45.085	16.58	- 81.0	Ethylamine, aminoethane
Dimethylamine	(5)	2	$(CH_3)_2NH$	45.085	6.88	- 92.19	None
Trimethylamine	(4)	3	$(CH_3)_3N$	59.112	2.87	-117.08	None
Diethylamine	(4)	4	$(C_2H_5)_2NH$	73.14	56.3	- 50.	None
Triethylamine	(4)	6	$(C_2H_5)_3N$	101.19	89.3	-114.7	None

derivatives were evaluated in terms of FID and ECD response characteristics. This work was limited to primary amines, and under optimum condidtions amines down to 10 picograms could easilty be quantified using an ECD detector. Clark and Wilk (15) used an ECD to evaluate the properties of halogenated amine derivatives. No increase in the sensitivity for the trifluoroacetyl amine derivatives using ECD was observed.

Mosier (16), et al quantitatively measured aliphatic amines volatilized from cattle feedyards. Direct gas chromatograph injection of acid solutions and GC separation of the pentafluorobenzoyl derivatives of the malodorous volatiles were used in identification. The derivatized amines were analyzed using a gas chromatograph equipped with an electron capture detector. The two columns used in this work were 6 percent DEGS and 10 percent Igepal CO 880.

Methylamine and ethylamine were detected in irradiated beef by Burks (17), et al. Several techniques, including colorimetric paper chromatography and gas chromatography, were used in quantifying results. Gas chromatogrphic determination of free mono-, di-, and trimethylamines in biological fluids was performed by Dunn (18), et al. A flame ionization detector was used to quantitatively separate the lower aliphatic amines. Separation of mono-, di-, and trimethylamine from extracts of fish tissue was achieved by Gruger (19).

Andrea (20), et al developed a precolumn inlet system for the gas chromatographic analysis of trace quantities of short-chain aliphatic amines. Losses inherent in the collection and direct gas chromatograph analysis of field air samples containing volatile amines necessitated an indirect analytical scheme. A teflon tube (3" x 5/16" OD) was filled with 20/30 mesh Ascarite and placed in the injector inlet of the gas chromatograph. Samples were collected in dilute sulfuric acid and aliquots were injected into the pre-column of the GC. Release of the free amines was found to be sufficiently reproducible for quantification of results. This technique avoided the problems encountered by Umbreit (21), et al, and Hardy (22) when using base loaded columns to analyze acidified aqueous solutions of amines from fish. The in situ release of the free amines from their salts produced a chromatographic column that changed with every injection. In addition, the column had a very short usable lifetime and lacked reproducibility after extended use.

Bowen (23) described a gas chromatograph procedure for the analysis of aromatic amines using an adsorption technique. Quantitative adsorption and desorption of aromatic amines using Tenax GC was demonstrated at the nanogram level. Samples were pulled through the Tenax GC trap for specific sampling periods, thermally desorbed at 250°C, and analyzed in a GC with a FID. The author recommended use of a NPD to increase sensitivity for aromatic amines on the tail of hydrocarbon solvents and eliminate venting the solvent.

PROCEDURAL DEVELOPMENT

From the results of the literature search it was determined that the analysis of the amines should be conducted by the use of gas chromatography.

A Perkin-Elmer Model 3920B gas chromatograph was dedicated for this purpose. This instrument has a dual/differential electrometer and has linear temperature programming capabilities along with a sub-ambient oven accessory. The instrument has been equipped with a flame ionization detector (FID), a nitrogen phosphorus detector (NPD), and an electron capture detector (ECD) and can be connected to a chemiluminescent detector. Of the specialty detectors available for the analysis of the amines, the NPD appeared to be the prime candidate and initial work was carried out using this detector. Because the amines are notorious for tailing and reacting with metal sites, a glass lined heated injector port and a glass interface were installed so that with the use of a glass column, the system would be glass throughout.

Lecture bottles of methylamine, dimethylamine, trimethylamine, and ethylamine, along with pure liquids of diethylamine and triethylamine, and a Tracor Model 412 Permeation Calibration System containing permeation tubes of all six amines were used as sources of the organic amines in the procedural development experiments. These sources allowed a method for preparing blends of varing concentrations of the organic amines.

Several column packing materials (all were developed especially for the analysis of amines) and column lengths were evaluated to determine which could provide the best peak separation with the shortest analysis time. The columns evaluated included: 12' x 1/4" glass columns packed with 28 percent Pennwalt 223 amine packing, a 6' x 4mm (id), 6' x 2 mm (id) and a 12' x 1/4" glass column packed with 4 percent Carbowax 20M and 0.8 percent KOH on Carbopak B, and a 6' x 4 mm (id) glass column packed with 2 percent KOH on Chromosorb 103. Several column temperatures, programming rates, and carrier flow rates (helium) were tried for each of the columns.

The best separation was accomplished using the 4 percent Carbowax 20M and 0.8 percent KOH on Carbopak B packing material in the 6' x 4 mm (id) glass column. This column would only partially separate dimethylamine and ethylamine under conditions which gave very broad peaks at long retention time. In order to increase sensitivity and shorten the analysis time an initial temperature of 130°C was chosen. At this temperature, the dimethylamine and ethylamine coalesce into a single sharp peak, and the analysis time is under 30 minutes.

The FID, NPD, and chemiluminescent detector were evaluated as detectors for the organic amines. The NPD was more sensitive than either the FID or the chemiluminescent detector. Also the NPD is only sensitive to compounds containing both carbon and nitrogen, eliminating many interferences that would be present using the FID.

In order to analyze automobile exhaust for the organic amines, it was found necessary to concentrate the amines in a trap or an absorbing reagent to obtain enough sample for a satisfactory analysis. Two collection procedures were evaluated, one in which the amines are collected in a trap filled with 1 gram Tenax-GC packing material, and another in which the amines are collected by bubbling the amines through an acid solution. There was some breakthrough of the amines through the Tenax-GC traps even at liquid nitrogen temperatures. Bubbling the amines through an acid solution proved to be the superior method for collecting the amines.

A sulfuric acid solution was found to effectively trap the amines at room temperature. To release the amines from the sulfuric acid solution into the GC column, an Ascarite loaded precolumn was installed into the injector block of the GC. This precolumn was found to work very well in releasing the amines into the GC column; however, the lifetime of the precolumn was found to vary from one injection to several hundred. The 4 percent Carbowax 20M and 0.8 percent KOH on Carbowax B packing material in the GC column was designed to be used with aqueous solutions and proved to be satisfactroy when used with aqueous sulfuric acid solutions.

The usefulness of the precolumn was usually terminated by the aqueous injections temporarily dissolving the Ascarite and the Ascarite redrying to form a plug, thereby preventing the sample from entering the column. Some time was spent on trying to determine why some precolumns lasted for only one injection while others for several hundred, but the results were inconclusive.

Poor injection repeatability resulted from a variety of problems. These problems included previous GC injection histroy, glass syringe purging technique, precolumn conditioning, and columneffects. Because of the problems mentioned above, and alternate method of analysis was evaluated. This method consisted of collecting the organic amines in glass impingers using dilute sufuric acid, converting the trapped amines to their pentafluorobenzayl chloride derivatives, and analyzing for these derivatives using a gas chromatography equipped with an electron capture detector. It was hoped that this method would (1) convert the amines to stable derivatives which would improve sample injection repeatability, and (2) provide improved detection limits with an electron capture detector.

This alternate procedure was found to be unsuitable for the detection of amines at the ppb levels. Tertiary amines (trimethyl- and triethylamine) cannot be detected by this procedure, and the secondary amines (dimethyl- and diethylamine) had a low sensitivity that made detection in the ppb range almost impossible. The peak areas of the primary amines (methyl- and ethylamine) were found to be time dependent. The GC peak areas of the methyl- and ethylamine derivatives were plotted against the time they were allowed to stand after initial mixing of the reagents to produce the derivatives. The mixing procedure is included in Table 6. The standing time includes 2 minutes of vigorous shaking (1 minute for the 1 minute test) plus any remaining time the mixture was allowed to stand at room temperature before injection into the GC. The effect of elapsed time on peak area is shown in Figure 9. This figure shows a rapid increase in peak area followed by a rapid decrease in the area. In order to obtain reproducible data at ppb levels, the injection time after mixing can vary by only seconds. Under normal operating conditions this would not be possible. Because of the time limitation, the procedure was abandoned for the quantitative analysis of the organic amines.

The GC-NPD procedure using the Ascarite precolumn has been reevaluated and most of the problems involved with its use have been solved. The inconsistent lifetime of the precolumn remains a problem in the procedure.

TABLE 6. MIXING PROCEDURE FOR PREPARATION OF PENTAFLUOROBENZOYLAMINE DERIVATIVES*

1. Pipette 1.0 mℓ of 0.01 N sulfuric acid containing 94 ppb methylamine and 220 ppb ethylamine into a 10 mℓ reacti-vial.
2. Pipette 3 mℓ of toluene into reacti-vial.
3. Pipette 1 mℓ of pentafluorobenzoyl chloride (PFBC) solution (50 μg PFBC in 100 mℓ toluene) into reacti-vial.
4. Pipette 1 mℓ of 10 percent aqueous potassium hydroxide solution into reacti-vial.
5. Shake and allow to stand for X minutes.

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* General procedure from private communication with Arvin R. Mosier, USDA, ARS, P. O. Box E, Fort Collins, Colorado 80521

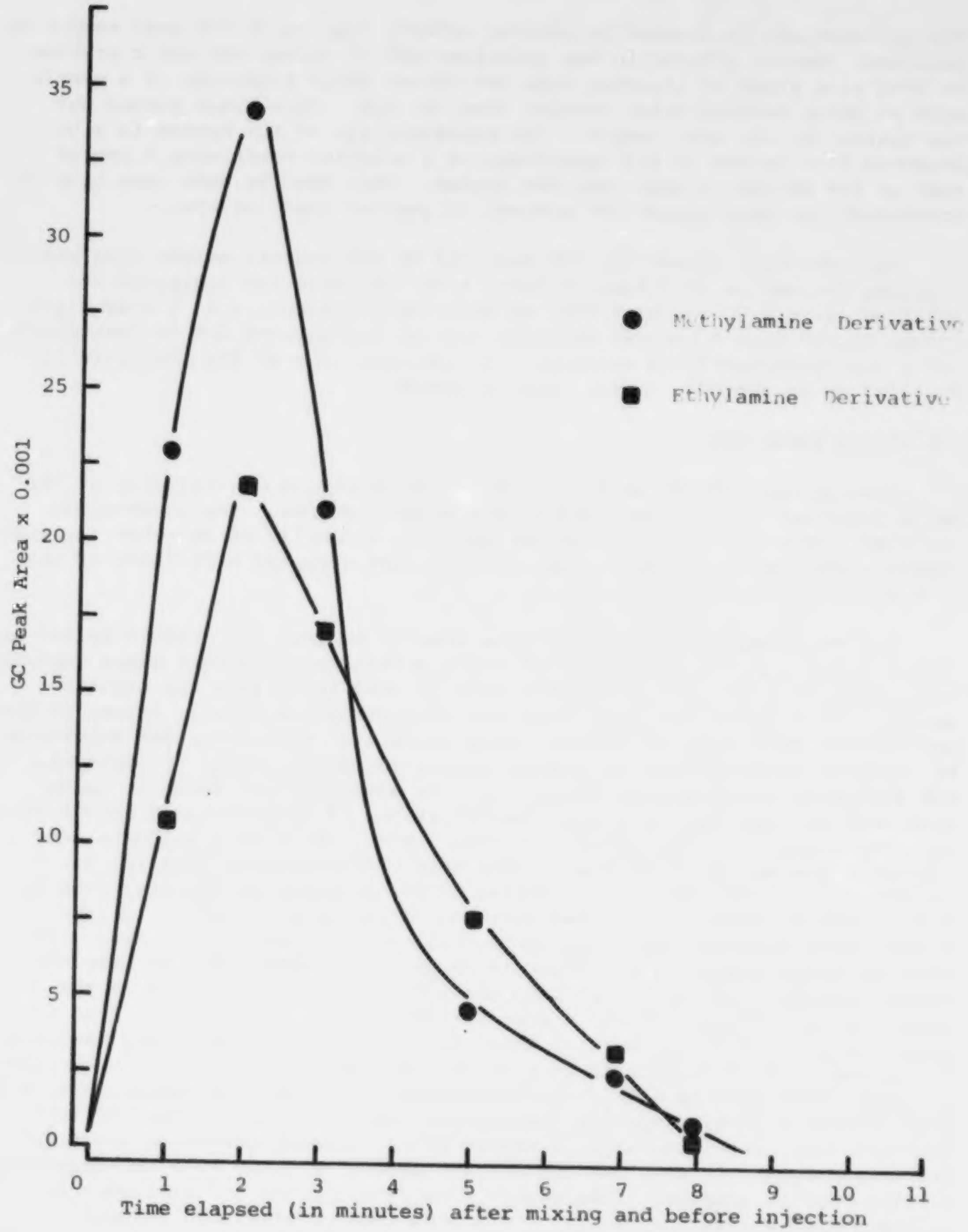

Figure 9. GC peak areas of pentafluorobenzoyl amine derivatives vs. time.

The syringes can be cleaned by purging several times with the next sample to analyzed. Memory effects in the precolumn and GC column are not a problem as long as a blank is injected into the system after injection of a sample with an amine concentration greater than one ppm. This blank purges out the system for the next sample. The repeatability of the system is also improved if a series of 4-5 injections of a solution containing 1 ppm of each of the amines is made into the system. This must be done each time the instrument has been unused for periods of greater than one hour.

The procedure chosen for the analysis of the organic amines consists of trapping the amines in dilute sulfuric acid solution and analyzing the solution using a GC equipped with an Ascarite precolumn, a 6' x 4 mm glass column packed with 4 percent Carbowax 20M and 0.8 percent KOH on Carbopax B, and a nitrogen-phosphorus detector. A finalized copy of the procedure is included as an appendix to the interim report.

VALIDATION EXPERIMENTS

Several experiments were carried out to determine the validity of the amine procedure for the analysis of the organic amines. The experiments included checks for GC injection variability, linearity of detector response, sample stability in the absorbing solution, and trapping efficiency of the 0.01 N sulfuric acid solution.

The finalized sampling conditions used to collect the organic amines are listed below, as is a discussion of their selection. A single glass impinger containing 25 mℓ of 0.01 N sulfuric acid is used to collect the organic amines. This single impinger traps 99+ percent of the organic amines at low ppm and ppb amine concentrations. This collection efficiency was determined by bubbling known amounts of organic amines through a series of impingers and analyzing each impinger separately. No advantage was found in using more than one impinger or higher concentrations of sulfuric acid except when the concentration of the amines exceeded 5 ppm. The 0.01 N sulfuric acid concentration was selected over higher acid concentrations (0.1 and 0.1 N) in order to prevent the neutralization of the ascarite in the precolumn any sooner than necessary. The concentration of the organic amines in exhaust should never approach the 5 ppm concentration; therefore, the single glass impinger containing 0.01 N sulfuric acid should be sufficient to trap the organic amines. Sulfuric acid was chosen over hydrochloric acid as the absorbing acid because of its higher boiling point. Hydrochloric acid is more volatile and could vaporize into the analytical column during analysis. During sampling, the impinger is kept in a 0°C ice bath. The ice bath offers no significant advantage in collection efficiency over room temperature, but does provide a stable sampling temperature during the test. The 0°C temperature also lowers the vapor pressure of the aqueous absorbing solution and thus prevents loss of any significant amount of water from the absorbing solution during sampling. The sample flow rate through the impingers is maintained at 4 liters a minute. This flow rate provides the largest amount of sample flow through the absorbing reagent without loss in absorbing efficiency or the physical loss of any absorbing reagent. A teflon sample line connecting the CVS to the impingers is heated to 77°C in order to prevent water from condensing in the sample line. The organic amines are water soluble, and the condensation of water in the sample line could cause a significant loss of sample in the sample line.

Samples have been found to be stable in the sulfuric acid absorbing solution for months. A two month standard containing 0.1 ppm of mono-, di-, and trimethylamine showed no significant decrease in concentration when compared to a freshly prepared standard. The absorbing solution is also stable over long periods of time with the only worry being contamination from any amines which might be present in the laboratory environment.

To determine the GC injection repeatability for the procedure over a wide range of concentrations, three standards containing 0.01, 0.1, and 1 ppm of mono-, di-, and triethylamine were prepared. Each standard was injected into the GC ten consecutive times. The area of each resulting peak was averaged over the ten runs and a standard deviation was calculated. The results of the injection repeatability experiments are presented in Table 7. Injections of the 0.01 N sulfuric absorbing solution were also made into the GC system. Peaks for monomethylamine and dimethylamine/monomethylamine (the two compounds give one peak in the procedure and are analyzed together as C_2H_7N) were detected in the absorbing solution and gave areas which corresponded to 50 percent of the area for the monomethylamine and dimethylamine in the 0.01 ppm standard and 20 percent of the monoethylamine in the 0.05 ppm standard. The procedure is not as sensitive to the ethylamines as it is to the methylamines; therefore, higher concentrations of the ethylamines (10, 1, 0.1 ppm) were used in the repeatability experiments. For the methylamines the injection repeatability improves with increasing concentration of the methylamines. The standard deviation for the 1 ppm standard containing mono-, di-, and trimethylamine is 5-6 percent, while the deviation for the 0.1 ppm standard is slightly higher at 7-8 percent. The standard deviation for the 0.01 ppm standard is even larger at 12-21 percent. Concentrations at or below 0.01 ppm of the methylamines are difficult to determine due to the poor injection repeatability and the interference from the absorbing solution. The injection repeatability follows no definite trend for the ethylamines. The standard deviations for mono-, di-, and triethylamine remain relatively constant at the three concentrations studied (0.1, 1, and 10): 7-8 percent for monoethylamine, 4-7 percent for dimethylamine, and 7-10 percent for triethylamine. Concentrations below 0.05 ppm of the ethylamines are difficult to determine due to the broadness of the diethylamine and triethylamine peaks and to the interference from the absorbing solution.

To determine the linearity of the nitrogen-phosphorus detector for each of the amines at the concentration ranges of interest, standard solutions containing 0.01, 0.05, 0.1, 0.5, and 1 ppm of mono-, di-, and trimethylamine, and 0.05, 0.1, 1, 5, and 10 ppm of mono-, di-, and triethylamine were prepared. These were made by weighing out required amounts of each of the organic amines-hydrochloric acid salts and dissolving them in the proper amount of sulfuric acid absorbing solution. Figures 10-15 show plots of the GC peak areas versus the concentration for each of the organic amines on a log-log scale. The relative GC areas for monomethyl-, dimethyl- and monoethylamine were corrected for the background peaks found in the absorbing solution. Mono-, di-, and trimethylamine give linear GC responses from

TABLE 7. INJECTION REPEATABILITY EXPERIMENTS

Amine	Concentration (ppm)	Average Area	Standard Deviation	Percent Deviation
Monomethylamine	1	8803	533	6.1
Monomethylamine	0.1	2004	134	6.7
Monomethylamine	0.01	1305	276	21.1
Dimethylamine	1	7081	372	5.3
Dimethylamine	0.1	1385	96	6.9
Dimethylamine	0.01	1006	117	11.6
Trimethylamine	1	5778	276	4.8
Trimethylamine	0.1	1044	87	8.3
Trimethylamine	0.01	344	46	14.2
Monoethylamine	10	10,943	977	8.4
Monoethylamine	1	8189	626	7.6
Monoethylamine	0.1	2748	178	6.5
Diethylamine	10	7025	483	6.9
Diethylamine	1	3460	134	3.9
Diethylamine	0.1	724	32	4.4
Triethylamine	10	10,921	1014	9.3
Triethylamine	1	5446	564	10.4
Triethylamine	0.1	1481	110	7.4

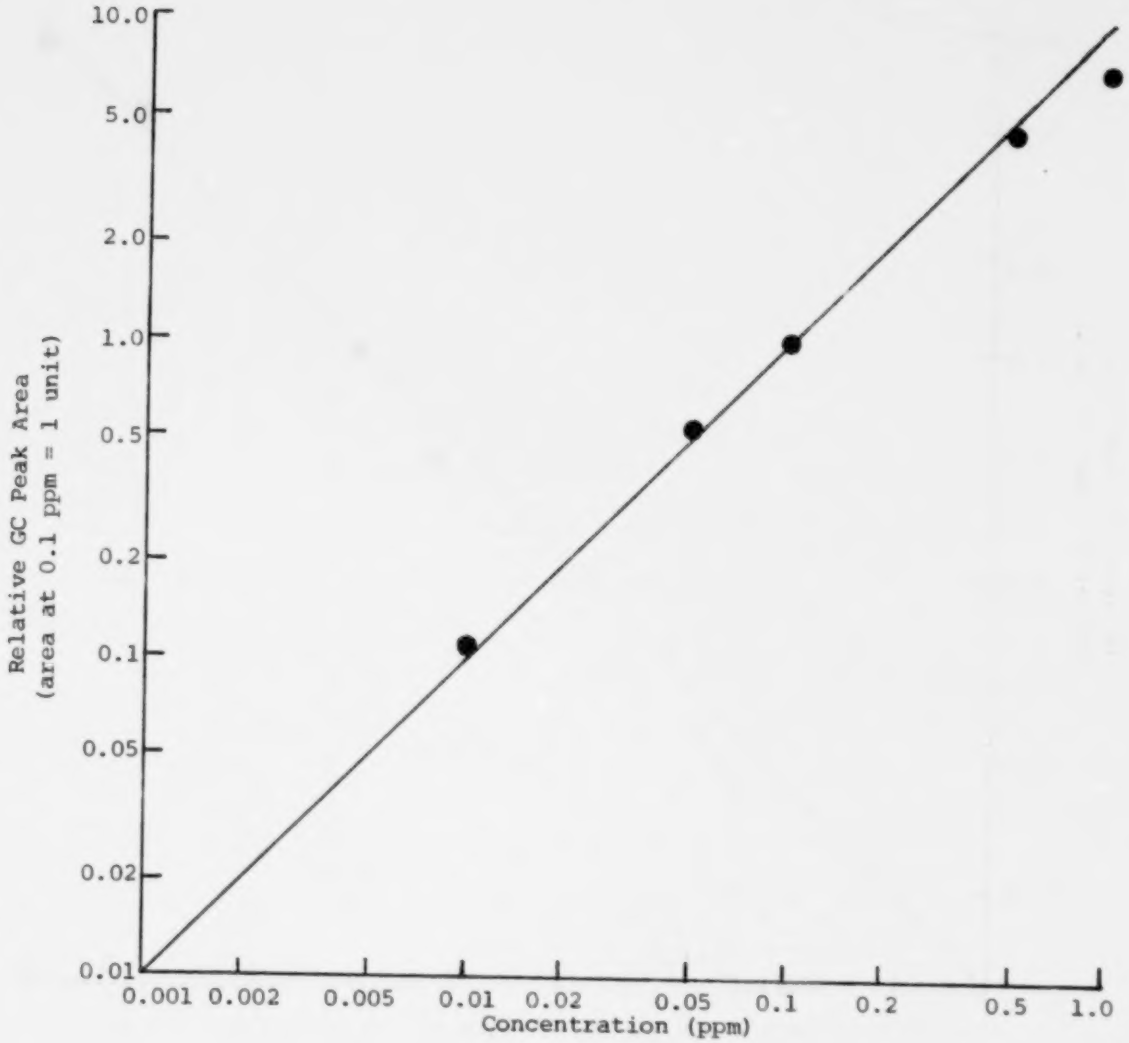

Figure 10. Linearity of monomethylamine GC Response
(plot on log-log scale).

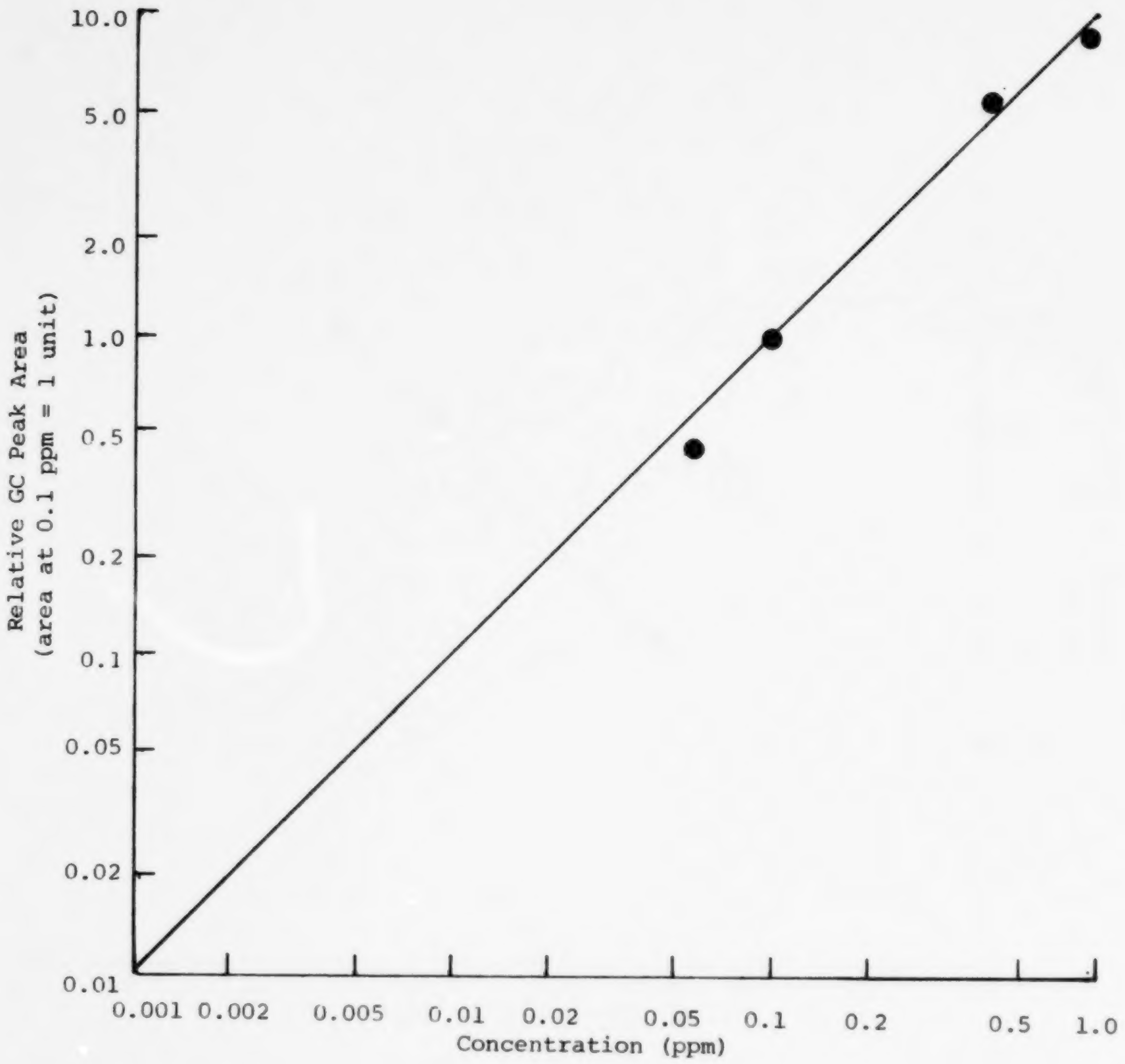

Figure 11. Linearity of dimethylamine GC response (plot on log-log scale).

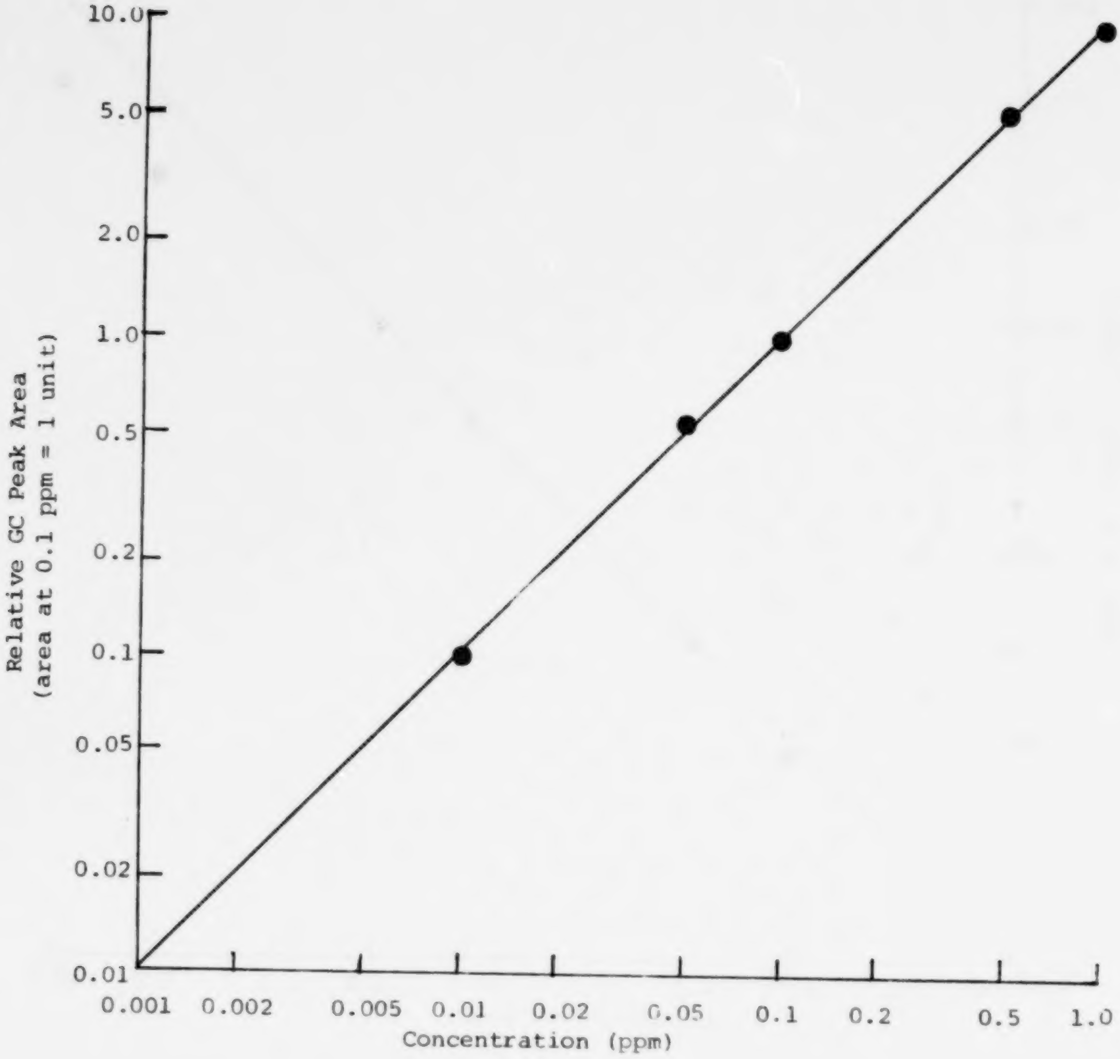

Figure 12. Linearity of trimethylamine GC response (plot on log-log scale)

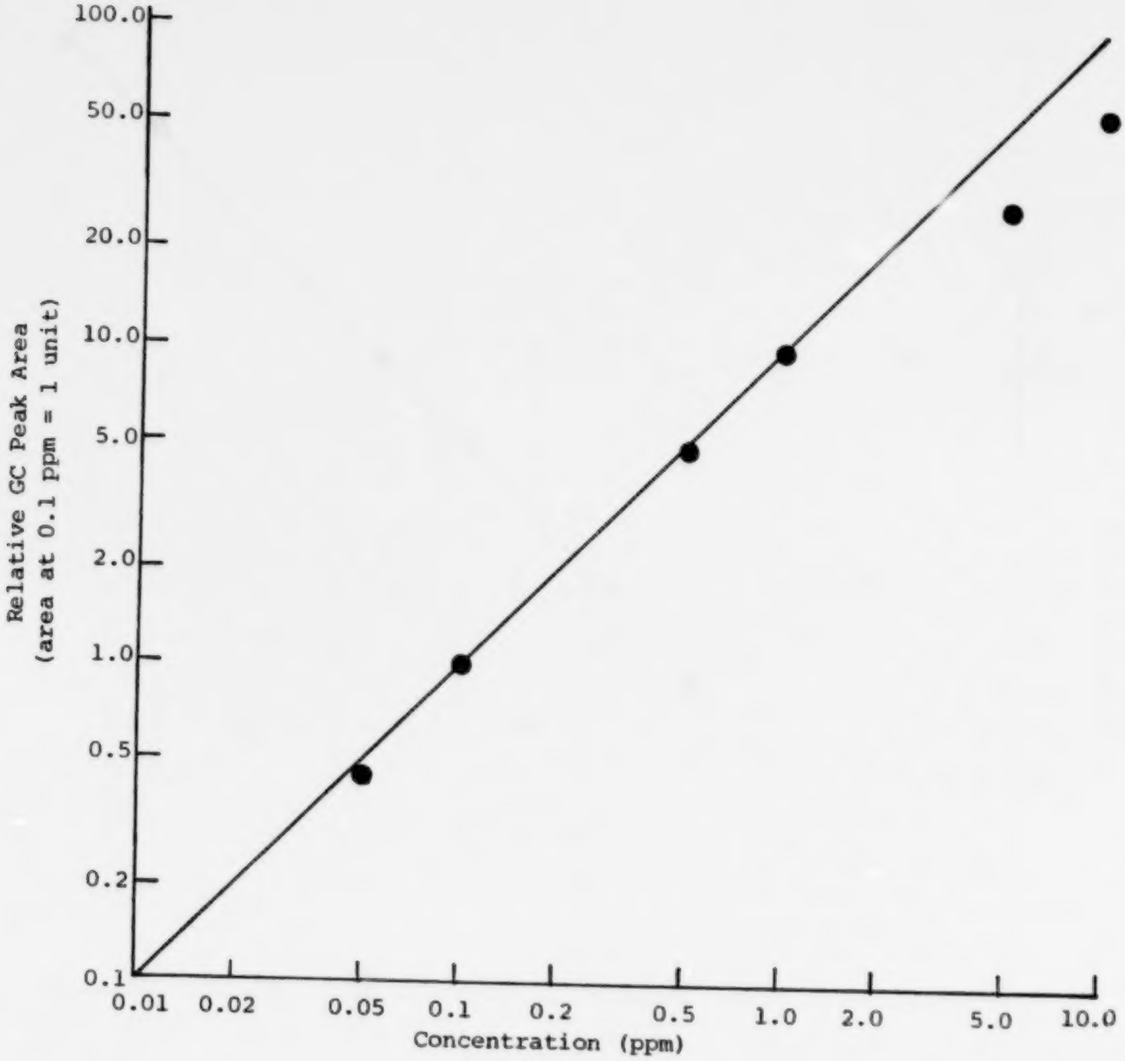

Figure 13. Linearity of monoethylamine GC response (plot on log-log scale).

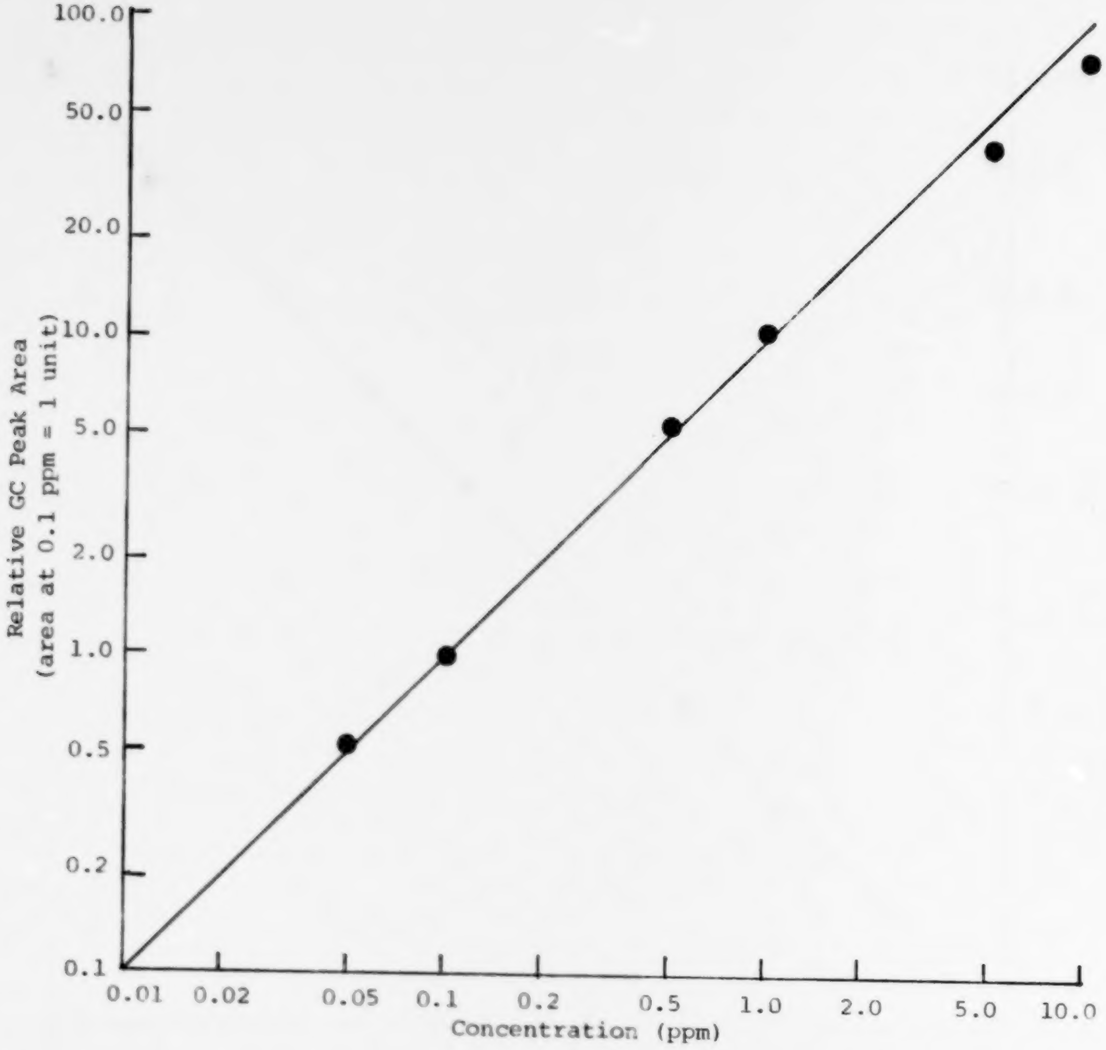

Figure 14. Linearity of diethylamine GC response (plot on log-log scale).

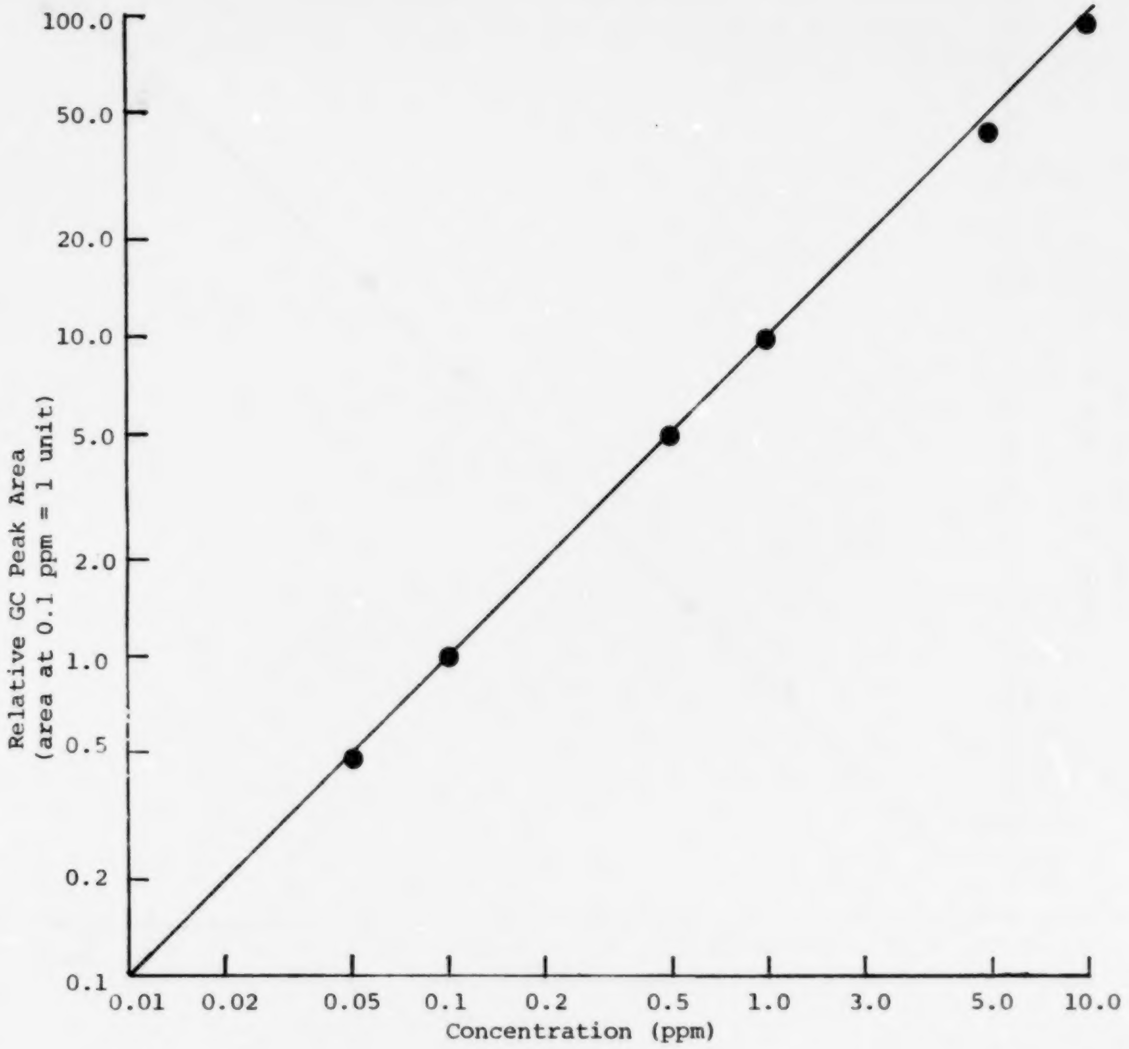

Figure 15. Linearity of triethylamine GC response (plot on log-log scale)

0.01 to 1 ppm and di-, and triethylamine give linear responses in the 0.05 to 10 ppm region. Monoethylamine gives a linear response from 0.05 ppm to 1 ppm, but shows some deviation from linearity in the 1.0 to 10 ppm range.

Ammonia at concentrations between 10-100 ppm in sulfuric acid does not give as large as a peak as does a 0.01 ppm solution of monomethylamine, and therefore does not present any major problems as an interference. However, the retention time (0.6 min) is close to that of monomethylamine (0.85 min) and care must be taken not to confuse one peak for the other. Acetonitrile (CH_3CN) has been found in exhaust at concentrations near the 0.1 ppm level. The NPD is sensitive to this compound and gives a peak in the chromatogram at a retention time of 1.8 minutes. This retention time is near that of trimethylamine (2.0 min) and care must be taken not to confuse the two compounds. No other compounds in exhaust have been found to be interferences in the procedure.

QUALIFICATION EXPERIMENTS

Injection experiments were carried out with three amines with the CVS tunnel. The amines included in this study were methylamine, dimethylamine and trimethylamine. A blend of the three amines was prepared in a spectra-seal aluminum cylinder, and this cylinder was used to inject the amines into the dilution tunnel.

A test sequence was developed to determine the injection recovery for the three methylamines. Three tests were conducted for the amines at ppm levels ranging from 0.12-0.19 ppm. Each test was conducted on a sequence basis with a 10 minute soak with the CVS off between each 30 minute collection interval. After the 10 minute soak of the third test, samples were collected to determine if the organic amines could be purged from the system. After the fifth test, this was extended to a two hour soak.

The results of the organic amine recovery experiments are presented in Table 8. As expected, the recovery of the methylamine was very low, 6-13 percent for the amine injections. Dimethylamine recovery increased from 18 to 36 percent recovery after three consecutive injections. Recoveries from trimethylamine were more reasonable with 76-93 percent recovery for three consecutive tests. Methylamine, dimethylamine, and trimethylamine could be detected in the tunnel even after three hours with the CVS blower on.

At this time, it is uncertain as to the precise reasons for the losses, but all possible steps have been made to preserve the integrity of the sampling system and the sample handling prior to injection into the gas chromatograph. It is doubtful that any substantial improvement could be made to the system without going to heating the tunnel, etc. The losses of the low molecular weight amines were not unexpected and these experiments confirmed those fears.

In summary, methyl- and dimethylamine had low recoveries in the tunnel without exhaust, and after CVS air purging of the tunnel, both amines were detected in measurable quantities. Trimethylamine recoveries improved with the number of consecutive injections and could be essentially purged after

TABLE 8. SUMMARY OF AMINE RECOVERIES (TUNNEL ONLY) AND TUNNEL HISTORY EFFECTS WITH METHYLAMINES

	Percent Recovery		
Test	0.19 ppm Methylamine	0.14 ppm Dimethylamine	0.12 ppm Trimethylamine
1 (amines injected)	6.2	18	76
10 min soak-CVS off			
2 (amines injected)	10.1	29	89
10 min soak-CVS off			
3 (amines injected)	13.1	36	93
10 min soak-CVS off			
4 (no amines injected)	2.0%*	4.8**	5.1%***
1 hour soak-CVS on			
5 (no amines injected)	2.5%*	3.7**	1.7%***
2 hour soak-CVS on			
6 (no amines injected)	1.1%*	2.6**	−0.3%***

Note: All sample collections were over a 30 minute test period. Tests 1-3 had amines injected whereas Tests 4-6 had only the CVS on.

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* based on amount of methylamine injected during Test 3

** based on amount of dimethylamine injected during Test 3

*** based on amount of trimethylamine injected during Test 3 three hours with the CVS on. Based on the results of these experiments, injection experiments with actual vehicle exhaust were not conducted.

RESULTS AND CONCLUSIONS

The concentration of organic amines in dilute exhaust can be determined by collecting the amines in 0.01 N sulfuric acid and analyzing the solution with a GC equipped with an ascarite precolumn and a nitrogen phosphorus detector. The amines are effectively trapped in 25 ml of 0.01 N sulfuric acid absorbing solution at a flow rate of 4 ℓ/min. For a twenty-three minute test and a sample flow rate of 4 ℓ/min, the procedure has a minimum detection limit of 2 ppb for each organic amine.

The accuracy of the procedure decreases as the concentration of the amine in the absorbing solution decreases. At a 0.01 ppm concentration of the organic amines in the absorbing solution, the percent standard deviation for the GC is 12-21 percent. The absorbing solution itself gives peaks equal to 0.005 ppm monomethylamine and dimethylamine/ethylamine. At the 0.01 ppm level or lower it is difficult or impossible to determine the concentration of amines. This concentration is equivalent to 2 ppb of the amines in dilute exhaust (23 minute test, sampling at 4 ℓ/min).

Acetonitrile and ammonia have been found in exhaust samples and give peaks in the chromatograms. Ammonia at concentrations of 10-100 ppm gives a peak approximately the size of a 0.01 ppm methylamine peak. The separation of the ammonia and the methylamine peak is 0.25 minutes, but the two can easily be distinguished if care is taken. Acetonitrile has a retention time that differs from trimethylamine by only 0.2 minutes, but the two can also be easily distinguished.

The amines are notorious for sticking to metal sites. The qualification experiments represent another example of this problem. The amines had low percent recoveries from the CVS dilution tunnel. The precent recovery increased directly as the number of injections into the tunnel increased. This phenomenon is probably due to the gradual coating of the tunnel with the amines, thus neutralizing the number of metal sites in the tunnel. With the CVS blower on the amines were slowly released from the tunnel up to three hours after the amine injections were made into the tunnel. It is possible that it the amines are present in concentrations of less than 0.1 ppm, the percent recovery may be very low or essentially zero. With this in mind, raw exhaust was sampled for organic amines on EPA Contract 68-03-2499 and the results were compared to the corresponding results for CVS diluted samples. The raw exhaust samples did not show a significant increase in the concentration of the organic amines when compared to the dilute exhaust samples. In most cases, no amines were detected in either raw or CVS diluted exhaust.

The organic amine procedure should provide a relatively accurate method for determining the concentration of the organic amines exiting the CVS tunnel; however, amine losses in the CVS tunnel must be taken into account when reporting these concentrations.

SECTION 4

SULFUR DIOXIDE PROCEDURE

LITERATURE SEARCH

At room temperature and atmospheric pressure sulfur dioxide is a highly irritating, nonflammable, and colorless gas. The gas is readily detectable at concentrations of 3-5 ppm by the human sense of smell. Physical properties of sulfur dioxide, SO_2 (sulfurous acid anhydride) include a freezing point of -75.5°C (1 atm), a boiling point of -10.0°C (1 atm), and a molecular weight of 64.063 (5).

The bulk of published literature regarding the analysis of sulfur dioxide has dealt with ambient air sampling. With the development of instrumental methods of analysis, the ability to measure sulfur dioxide in stationary and mobile source exhausts now exists. The following review of references reveals a wide variety of analytical techniques used in the measurement of sulfur dioxide concentrations.

A frequently used method for the analysis of sulfur dioxide is a colorimetric method. The most commonly employed colorimetric technique is the West-Gaeke method (24-28). This method has been collaboratively tested, with the lowest concentration range studied being well above the levels most frequently found in rural and global background air (29).

A modified version of the West-Gaeke method involves the collection of sulfur dioxide in 0.1M sodium tetrachloromercurate(II) (TCM). Sulfur dioxide reacts with the TMC to form a dichlorosulfitomercurate complex (DCSM). In this modified version, the DCSM resists oxidation by oxygen in the air and oxygen dissolved in the absorbing solution. Ethylenediamine tetracetic acid disodium salt (EDTA) is added to the TCM absorbing solution to complex any heavy metals that could oxidize sulfur dioxide before the DCSM is formed (30,31), and sulfamic acid is added to the absorbing solution to destroy any interfering nitrite ion which might be present (32).

The colorimetric determination of sulfur dioxide is based upon the measurement of the red-violet color produced by the reaction of DCSM with hydrochloric acid, pararosaniline and formaldehyde. The effect of the pararosaniline dye purity on the colorimetric procedure has been reported by several researchers (33,34). Since the dye purity does effect the results of the colorimetric procedure, various techniques for the purification of commercial grade pararosaniline have been published (25,27,35), and pararosaniline purified especially for the colorimetric analysis of sulfur dioxide is commercially available (35).

A major potential source of error associated with the West-Gaeke colorimetric method for measuring sulfur dioxide is the widely differing collection efficiency reported for Greenburg-Smith and midget impingers at low sulfur dioxide concentrations (36). Urone, et al, investigated the collection efficiency of a TCM solution by the use of microgram quantities of sulfur dioxide tagged with ^{35}S (37). In this investigation, it was found that a series of bubblers cannot be used to determine absorber collection efficiency. Bostrom observed a 99 percent collection efficiency for a concentration range 100-1000 ppb sulfur dioxide in a TCM solution (38).

Work has been conducted in the development of other colorimetric methods for the analysis of sulfur dioxide. Attari developed a procedure whereby sulfur dioxide is absorbed into a solution of ferric ammonium chloride, perchloric acid, and phenanthroline dye (39). A color complex with an absorbance of 510 mm was formed, and although the color developed within 10 minutes, it tended to fade with time. Hydrogen sulfide was found to be an interference in the procedure.

Kawai used the reaction of barium chloranilate with sulfate as an indirect measurement of sulfur dioxide (40). Sulfur dioxide was absorbed in a solution containing hydrogen peroxide and barium chloranilate. Barium chloranilate reacts with the sulfate ion producing a red-violet chloranilic acid ion. Although this method may be satisfactory for flue gas analysis, it lacks the sensitivity required for ambient air analyses.

Conductivity methods have been used for continuously monitoring sulfur dioxide in air (41). The conductivity of a dilute sulfuric acid-hydrogen peroxide reagent changes due to the absorption of pollutants. This change in conductivity is assumed to result primarily from sulfur dioxide absorbed from the sampled air and oxidized to sulfuric acid. In many cases, sulfur dioxide is the major pollutant present; however, if other pollutants are present, their collection efficiency and solubility may be significantly different than for sulfur dioxide. Several field comparisons of conductivity with other sulfur dioxide procedures indicate a fair agreement (42-47). Hydrochloric acid gas, ammonia, and chlorine substantially increase conductivity. Shikiya and McPhee found two- to fourfold differences between different conductivity analyzers and between conductivity and colorimetric analyzers (44). Although the conductivity procedure may be acceptable for point sources of sulfur dioxide in isolated areas, its high potential for positive and negative interferences limits its application.

Iodometric methods were among the first adapted for air pollution analysis from the industrial hygiene litereature. With this method, the sulfur dioxide is collected in an impinger containing a standard NaOH. The absorbing solution is acifified and the liberated sulfurous acid is titrated with standard iodine solution (45). Another method employs a standard iodine-potassium absorbing solution (46). Iodometric methods of analysis for sulfur dioxide generally suffer from a lack of sensitivity and interferences from hydrogen sulfide.

Adsorption sampling methods have also been developed for the measurement of sulfur dioxide (48). Sulfur dioxide is adsorbed on silica gel, desorbed, and reduced to hydrogen sulfide at 700-900°C over a platinum catalyst. The hydrogen sulfide is then absorbed in a 2 percent ammonium molybdate solution and determined colorimetrically. Although this technique is relatively specific for sulfur dioxide, the final colorimetric determination by the molybdenum complex does not utilize the most sensitive method available.

In addition to the aforementioned techniques, sulfur dioxide has been measured by filtration (49-53) and static collectors (54-60). Air samples are passed through potassium bicarbonate impregnated filters and analyzed for sulfate. The collection efficiency of these filters is dependent upon humidity, temperature, and the atmospheric concentration of sulfur dioxide. The lead peroxide candle static collector was developed by Wilson and McConnell as an inexpensive method for measuring relative "sulfation" of the atmosphere (54). The sulfur dioxide collection efficiency is dependent upon temperature, relative humidity, wind speed, atmospheric concentration of sulfur dioxide, and the length of exposure period (55). Ikeda determined ambient sulfur dioxide levels by collecting samples on active carbon filters, washing the filters with distilled water, and titrating with barium chloranilate.

With the advent of modern instrumental methods of analysis, specifically gas and ion chromatography, a substantial amount of data has been published. Most trace gas analysis for sulfur dioxide has been conducted using gas chromatographs with flame photometric detectors (FPD) (61-70). The FPD is highly selective for sulfur compounds and has low minimum detection limits. Analysis for sulfur dioxide is generally performed using all teflon or glass systems. Sulfur dioxide will react with active sites in the gas chromatograph system, making the use of inert materials essential for trace quantitative analysis. Gas chromatographs with FPD and linearizing circuitry provide a wide dynamic range for ambient and source sulfur dioxide levels. In some instances, the collection technique precludes the use of GC-FPD techniques; i.e., bag sampling from dilute automotive exhaust or source sampling. The use of gas chromatography would be a prime candidate if the sample integrity could be assured in the sample acquisition and subsequent analysis.

A more resent development in methods of analysis for sulfur dioxide involves the use of ion chromatograph (71). This technique involves collection in a hydrogen peroxide absorbing reagent and measurement of the resulting sulfate ion using ion chromatography. Ion chromatography is a specialized area of liquid chromatography which will separate and quantify the individual cations or anions. This technique has been applied to the measurement of sulfur dioxide in ambient air, and adaptation to dilute automotive exhaust should not be difficult.

Other instruments are commercially available that are reported to measure sulfur dioxide in ambient or dilute automotive exhaust. Such instruments include continuous detection by pulsed fluorescent UV and second derivative UV analyzers. A pulsed fluorescent UV analyzer for sulfur dioxide was found to give recoveries on the order of 115-125 percent, indicating that a positive interference is present (72). The second derivative

UV sulfur dioxide analyzer has inherent problems when being used on continuous samples. The mirrors are located in the actual cell and become coated with various exhaust components even after filtration of the sample. The mirrors will become etched and need resurfacing if the unit is used in the presence of sulfur dioxide, sulfate ion, or other corrosive exhaust components. The inherent noise level, along with the consistent mirror problem, preclude the use of a second derivative UV analyzer for measuring sulfur dioxide on a continuous basis.

A variation of the GC method for measuring sulfur dioxide is the use of a continuous analyzer using an FPD detector. Although this approach is good in theory, it has several problems associated with the performance of the FPD detector. These units were originally designed to monitor sulfur dioxide levels in the ambient air and adaptation to automotive exhaust was not straightforward. Air samples had essentially the same oxygen and nitrogen levels all of the time; however, dilute exhaust samples have variable carbon dioxide, oxygen and nitrogen concentrations. The species have been found to cause quenching effects on a FPD detector. With the constantly changing carbon dioxide, oxygen, and nitrogen it would be impossible to correct for any quenching effect. The use of a continuous FPD analyzer for measuring sulfur dioxide in automotive exhaust would not be acceptable unless the quenching effects could be eliminated.

PROCEDURAL DEVELOPMENT

From the results of the literature search it was determined that the analysis of sulfur dioxide should be conducted by the use of ion chromatography. An ion chromatograph built at Southwest Research Institute was dedicated for this purpose. This instrument utilizes a modified Swagelok reducing union for a conductivity cell, a Hall conductivity detector, a Milton Roy mini-pump, a Soltec multivoltage recorder, a Glenco Scientific pulse dampener, and polyethylene cubitainers from Cole Parmer Instrument Company for the analysis of sulfur dioxide. A minimal amount of procedural development work was necessary for this procedure; however, several instrument and sampling parameters did have to be determined. The selection of these parameters are discussed in detail in the Validation Experiments section.

In order to analyze automotile exhaust for sulfur dioxide, a trap or an absorbing reagent must be used to concentrate the sulfur dioxide. A method which has been previously used at Southwest Research Institute for collecting and concentrating sulfur dioxide was selected and validated for use in this project. This method consists of bubbling dilute exhaust through a dilute aqueous hydrogen peroxide solution. The hydrogen peroxide reacts with the sulfur dioxide to give sulfate ion which remains in the absorbing solution.

The parameters selected for the analysis of sulfur dioxide are listed below. The sulfur dioxide from the exhaust is bubbled through two impingers (maintained at ice bath temperatures) in series with each impinger containing 25 mℓ of a 3 percent hydrogen peroxide solution. The exhaust flows through the impingers at a rate of 4ℓ/min. The two impingers together trap 99 percent of the sulfur dioxide present in exhaust. A 0.5 micron Fluoropore filter is installed in the sampling line prior to the bubblers to remove particulate which could contaminate the separator column during analysis. A portion of the absorbing solution is loaded into the sample loop and injected into the ion chromatograph. For analysis the ion chromatograph utilized three columns and an eluent composed of 0.003M $NaHCO_3$ plus 0.0024M Na_2CO_3. The eluent flows at 30 percent of full pump capacity through a 3 x 150 mm precolumn (this column helps prevent contamination of the separator column), a 3 x 500 mm separator column and a 6 x 250 mm suppressor column packed with AG-1-x10 anion suppressor resin (this neutralized the ionic effect of the eluent while increasing that of the sample ion). A finalized copy of the procedure is included as an appendix to the interim report.

VALIDATION EXPERIMENTS

Sulfur dioxide validation experiments were performed to verify the sampling and instrument parameters. These experiments involved the determination of sampling flowrate, sampling temperature, kind and concentration of absorbant, and number of bubblers required to collect 100 percent of the sulfur dioxide. The variables associated with the ion chromatograph that were determined included type and concentration of eluent, injection loop size, flowrate, injection variability, and linearity of response. In addition to determining sampling and instrument parameters, validation experiments were performed to verify certain portions of the ion chromatographic procedure for sulfur dioxide analysis. Tests for interferences, sample stability, and standard stability were among those conducted. Also, the method of washing glassware and the effect of combining the contents of the two bubblers for analysis were studied.

A number of possible interferences were tested by bubbling the suspected gas at 4 ℓ/min through three bubblers in series. Each bubbler contained 25 mℓ of 3 percent hydrogen peroxide and was maintained at ice bath temperatures (0-5°C). The tests lasted approximately twenty minutes each. The results are shown in Table 9. In the zero air, zero nitrogen, 3 percent CO_2 and 100 ppmc HC tests, no detectable amount (less than 0.01 ppm SO_2) was found. A positive interference of 0.01 ppm SO_2 was produced in the 100 ppm NO_x test. The greatest interference, 0.02 ppm SO_2, was found in the 100 ppm CO test. Another source of interference was caused by the sulfuric acid-chromic acid bath in which the bubblers were washed. The sulfate ion from the sulfuric acid could not be sufficiently rinsed from the bubblers, even with repeated deionized water rinses. For this reason, a 1:1 (v:v) nitric acid and water solution was used to wash the bubblers used in the sulfur dioxide procedure. The sulfate present in the hydrogen peroxide absorbant caused a positive interference that could be corrected by subtracting the sulfate value of a background sample and from the sulfate value of an exhaust sample.

Another test which was conducted to verify the SO_2 procedure was the combining of the contents of both bubblers for analysis on the ion chromatograph. Table 10 shows the results of this experiment and compares these values to those obtained by separate analysis of the contents of each bubbler. The SO_2 concentrations calculated at the 1 x 30 attenuation setting

TABLE 9. INTERFERENCES TO SO_2 ANALYSIS

Suspected Interference	Concentration SO_2 (ppm SO_2) Bubbler 1	2	3	Total SO_2 (ppm)
Zero air	0.00	0.00	0.00	0.00
Zero N_2	0.00	0.00	0.00	0.00
3% CO_2-run 1	0.00	0.00	0.00	0.00
3% CO_2-run 2	0.00	0.00	0.00	0.00
100 ppmc HC	0.00	0.00	0.00	0.00
100 ppm NO_x	0.01	0.00	0.00	0.01
100 ppm CO	0.01	0.01	0.00	0.02

TABLE 10. ANALYSIS OF THE CONTENTS OF BUBBLERS 1 AND 2 SEPARATELY AND COMBINED

Sample	Attenuation	Separate Analysis (ppmSO_2)	Combined Analysis (ppmSO_2)	% Difference
1	1 × 30	0.60	0.94	57.4
2	1 × 30	0.55	0.64	16.1
3	1 × 30	0.52	0.51	2.1
		AVERAGE 0.56	0.70	25.0
4	100	2.00	2.40	19.9
5	100	2.03	2.44	19.8
6	100	2.02	2.42	20.1
		AVERAGE 2.02	2.43	20.3

were from an SO_2 baseline produced by a noncatalyst 1972 Plymouth Fury equipped with a 360 V8 engine. The concentrations at the 1 x 100 attenuation setting were obtained from sulfur dioxide recovery experiments using the same test car. The combined baseline values in Table 10 are between 2 percent and 57 percent higher than the separately analyzed samples, with the average being 25 percent. The recovery values for the combined bubblers in the recovery tests also ran about 20 percent higher than the separately analyzed bubbler samples. Because of the dilution problems encountered when combining the contents of both bubblers, each bubbler is analyzed separately. The last validation experiment for the ion chromatographic method of sulfur dioxide analysis involved determining the stability of samples and standards over a period of time. The sulfuric acid standards made up in filtered deionized water remained stable for at least fourteen weeks. Sulfate standards made up from stock solutions prepared on 11/30/77 and 3/13/78 were analyzed on 3/13/78 and the peak areas were compared. The results, shown in Table 11, indicate that the fourteen week old standards repeated within 10 percent of the freshly prepared standards. A study was also conducted with a variety of samples of different ages to determine sulfate longevity in the 3 percent hydrogen peroxide absorbant. One week after collection and initial analysis a sample obtained from an SO_2 exhaust recovery experiment remained at 0.13 ppm SO_2. A two week old 0.06 ppm SO_2 baseline sample produced similar results. There was no change observed in the sulfur dioxide level. A tenth

TABLE 11 SULFATE STANDARD STABILITY

Standard Concentration $(\frac{\mu g SO_4^{-2}}{m\ell})$	Standard Preparation	Attenuation	Height (in)	Amplitude	% Difference
0.96	(11/30/77)	3	4.73	125,844	0.6
0.96	(03/13/78)	3	4.77	125,080	
4.80	(11/30/77)	10	7.72	148,259	0.6
4.80	(03/13/78)	10	7.62	147,300	
9.60	(11/30/77)	30	5.41	130,852	0.1
9.60	(03/13/78)	30	5.45	131,036	
38.40	(11/30/77)	100	7.93	149,864	0.8
38.40	(03/13/78)	100	7.81	148,668	
96.00	(11/30/77)	300	6.09	135,666	0.0
96.00	(03/13/78)	300	6.08	135,638	

week collection efficienty sample, however, did vary from its initial concentration of 0.13 ppm by decreasing 7.9 percent to 0.12 ppm SO_2. This is greater than the injection repeatability of 1.2 percent, however, within the minimum detection limit of 0.01 ppm SO_2. The samples appear to be stable at least two weeks but less than ten weeks, the break-off point probably lying between four and six weeks.

The second portion of validation testing included the determination of SO_2 sampling parameters. Nominal concentrations of 5 and 12 ppm SO_2 were collected for 20 minutes in three bubblers, each containing 25 mℓ of 3 percent hydrogen peroxide. The results of these tests are shown in Table 12.

TABLE 12. SO_2 COLLECTION EFFICIENCY AS A FUNCTION OF FLOWRATE AND TEMPERATURE

Test	Flow-rate (ℓ/min)	Temp, (°F)	SO_2 Concentration (ppm) and (%) in bubbler			Bubbler 1+2+3 (ppm)	% SO_2 trapped in bubblers 1 and 2
			1	2	3		
				Nominal 5 ppm SO_2			
1	4	72	4.31(95.3)	0.16(3.4)	0.06(1.3)	4.52	98.7
2	4	32	6.73(96.7)	0.17(2.4)	0.06(0.1)	6.96	99.1
3	2	32	6.48(94.6)	0.21(3.1)	0.16(2.3)	6.85	97.7
4	2	75	6.71(98.8)	0.12(1.8)	0.09(1.4)	6.93	98.6
				Nominal 12 ppm SO_2			
5	4	32	22.4(92.5)	1.25(5.2)	0.54(2.2)	24.2	97.7
6	4	32	24.8(99.1)	0.13(0.5)	0.09(0.4)	25.0	99.6
7	4	32	28.5(99.0)	0.22(0.8)	0.07(0.2)	28.8	99.8
8	4	32	29.3(97.8)	0.35(1.2)	0.30(4.0)	29.9	99.0
9	4	32	30.0(98.5)	0.24(0.8)	0.21(0.7)	30.4	99.3
10	4	32	21.2(97.9)	0.20(0.9)	0.25(1.2)	21.7	98.8
11	4	32	29.9(98.5)	0.23(0.8)	0.23(0.8)	30.4	99.3
12	4	32	28.9(98.5)	0.32(1.1)	0.12(0.4)	29.3	99.6

The largest quantity of sulfur dioxide was retained at a flowrate of 4 ℓ/min at ice bath temperature. 99.1 percent SO_2 was collected in the first two bubblers under those conditions. It is desirable to prevent small particulate debris in the exhaust from entering the samples and, thus, the columns of the ion chromatograph. If this form of contamination is allowed to collect in the columns the liquid flow becomes hampered causing increased backpressure. To avoid this problem each day a fresh 0.5 micron Fluoropore filter is inserted in the sampling line prior to the bubblers. Tests were conducted with and without filters in the sampling line to see if any sulfur dioxide was retained on the filter. An unfiltered baseline sample produced by the Plymouth Fury test car was compared with two filtered baseline samples from the same car. The filtered samples, averaging 0.44 ppm SO_2 ran 6.8 percent higher than the unfiltered sample (0.41 ppm), a difference of 0.03 ppm SO_2. Sulfur dioxide recovery from the exhaust of the same test car ran 1.5 percent lower for the filtered sample (1.35 ppm SO_2) compared to the unfiltered sample (1.37 ppm SO_2). The difference for these exhaust recovery samples was 0.02 ppm SO_2.

The third portion of validation testing involved the determination of instrument parameters; eluent concentration and flowrate, columns, sample loop size, linearity of response and injection variability. Choice of eluent concentration and flowrate will depend on the columns chosen and the species present in the samples. Exhaust samples contain a variety of amines, fluoride, chloride, nitrite, phosphate, nitrate and sulfate. Nitrate elutes just prior to sulfate necessitating the use of an efficient separator column. A 3 x 500 mm glass column packed with patented resin is the separator column chosen for sulfate analysis. The suppressor column is a 6 x 250 mm glass column with AG 50W-X16 resin. A 0.003M $NaHCO_3$ and 0.0024M Na_2CO_2 eluent solution flowing at 30 percent of pump capacity gives good baseline resolution when a 500 μℓ sample loop is used. Another instrument factor which needed to be determined was the injection variability.

The ion chromatograph has an injection repeatability of 1.1 or 1.2 percent as shown in Table 13. This is represented by C_v (coefficient of variation) which is the standard deviation divided by the mean and multiplied by 100. The mean or average is represented by $\bar{x}$ and standard deviation of S_x. For these calculations peak heights instead of peak areas were used since the heights repeated much better and with greater precision than the areas.

Two different standards were analyzed: $0.5 \frac{\mu g\, SO_4^{-2}}{m\ell}$ and $4.0 \frac{\mu g\, SO_4^{-2}}{m\ell}$.

The final instrument parameter determined was the linearity of response of sulfate standards at different attenuations. The sulfate standards, made up from sulfuric acid and filtered deionized water, maintained linearity at each attenuation but the slopes became steeper as the sensitivity decreased. Table 14 shows heights corresponding to each standard used and Figure 16 shows the graphical representation of the data. At the 1 x 10 scale setting, the relative slope was 1.7, at the 1 x 30 setting it was 2.5 and at the 1 x 100 setting the slope was 2.6. It was not necessary to cary the curve any further, since no samples have been obtained that fall in the higher concentration range. However, it was found that linearity was maintained at concentrations from 40 to 100 $\frac{\mu\ell\, SO_4^{-2}}{m\ell}$.

QUALIFICATION EXPERIMENTS

Qualification tests were conducted on the same test car from which validation data was obtained. This test car was a noncatalyst 1972 Plymouth Fury equipped with a 360 V8 engine. A baseline was run on the car to

TABLE 11 INJECTION REPEATABILITY FOR ION CHROMATOGRAPH

Sample	Concentration $\left(\frac{\mu g SO_4^{-2}}{m\ell}\right)$	Attenuation	Height (in)
1	3.84	1 × 10	5.37
2	3.84	1 × 10	5.43
3	3.84	1 × 10	5.51
4	3.84	1 × 10	5.45
5	3.84	1 × 10	5.50
6	3.84	1 × 10	5.53
			$\bar{x}$ 5.46 in
			S_x 0.06 in
			C_v 1.1%
7	0.48	1 × 10	0.81
8	0.48	1 × 10	0.80
9	0.48	1 × 10	0.79
10	0.48	1 × 10	0.81
11	0.48	1 × 10	0.80
12	0.48	1 × 10	0.81
			$\bar{x}$ 0.80 in
			S_x 0.01 in
			C_v 1.2%

TABLE 14. CALIBRATION CURVE FOR SULFUR DIOXIDE

Standard Concentration ($\frac{\mu g NH_4^+}{m\ell}$)	Attenuation	Height (in)	Heights Corrected to 1 × 10 scale (in)
0.48	1 × 10	0.85	
0.96	1 × 10	1.87	
1.48	1 × 10	2.38	
1.92	1 × 10	3.23	
2.88	1 × 10	4.89	
3.84	1 × 10	6.62	
4.80	1 × 10	8.16	
4.80	1 × 30	2.60	7.80
7.68	1 × 30	4.77	14.31
9.60	1 × 30	6.49	19.47
19.20	1 × 100	3.37	33.70
28.80	1 × 100	6.15	61.50
38.40	1 × 100	8.32	83.20

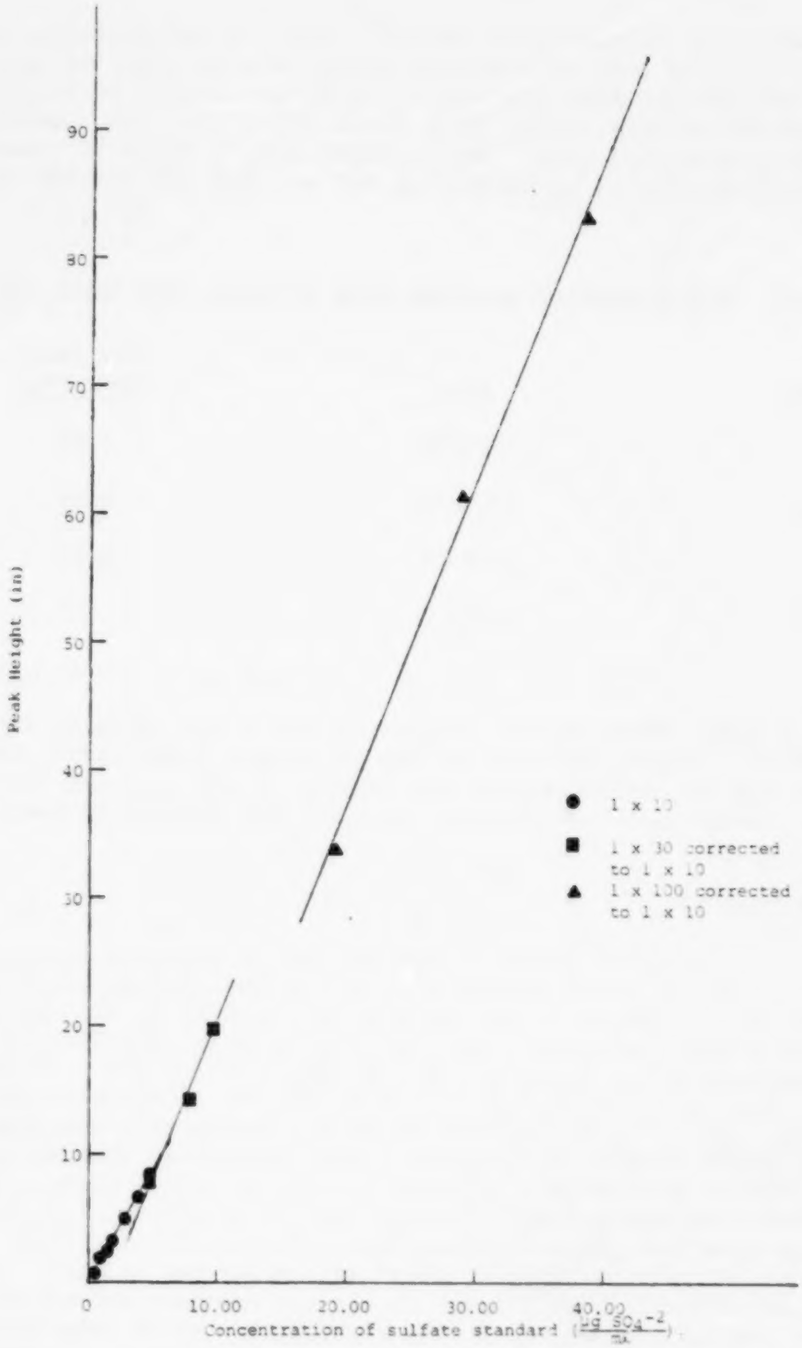

Figure 16. SO_2 calibration curve.

determine SO_2 emissions of the car by itself. First, a concentration of 500 ppm SO_2 was injected into the constant volume sampler (CVS) without exhaust for 31 minutes and then into the CVS with the exhaust of the test car during a hot FTP driving cycle. From these injections, the recovery of SO_2 was determined from each test. The baseline data in Table 15 shows that an average of 0.49 ppm SO_2 is produced from the car when the hot FTP driving cycle is run.

TABLE 15. SULFUR DIOXIDE BASELINE FROM PLYMOUTH FURY TEST CAR

Test	Date	SO_2 Conc. (ppm SO_2)
1	2/27/78	0.66
2	3/06/78	0.45
3	3/06/78	0.42
4	3/06/78	0.43
	Average =	0.49 ppm SO_2

The SO_2 recovery tests show that 101 percent of the sulfur dioxide injected into the CVS alone survives the trip to the collection point (Table 16) and 99.7 percent of the SO_2 injected into the exhaust of the test car (Table 17) is recovered. These values essentially represent 100 percent recovery in both instances.

RESULTS AND DISCUSSION

The ion chromatographic method of sulfur dioxide analysis is a simple, sensitive and relatively rapid procedure with a minimal number of interferences. Zero air, nitrogen, 3 percent CO_2 and 100 ppmc HC did not interfere within the minimum detection limit of 0.01 ppm SO_2. However, 100 ppm NO_x and 100 ppm CO produced positive interferences of 0.01 and 0.02 ppm SO_2, respectively. The sulfuric acid-chromic acid bath which had been previously used to wash the bubblers also provided positive interference for samples collected in bubblers washed in this bath. The problem was averted by replacing the sulfuric acid-chromic acid with 1:1 (v:v) nitric acid. The manufacturer has also stated that persulfite will interfere with sulfate analysis and that oxylate ion will interfere if the separator column capacity is reduced. No problem has been noted with these two species. The decision to analyze the samples in each of the two bubblers separately rather than in combination was due to the results of a study comparing the two methods. It was discovered that a 20-25 percent increase in sulfate concentration occurs when the samples from a set of bubblers are combined. This is apparently a dilution problem that can be avoided by analyzing each sample separately.

The effect of age on sulfate standards and samples was investigated

TABLE 16. SULFUR DIOXIDE RECOVERY FROM DIRECT CVS INJECTION

	Nominal Flowrate (ft^3/min)		SO_2 Injected		SO_2 Recovered			
Test	SO_2	CVS	Vol. SO_2 Injected (ft^3)[b]	Conc. SO_2 Injected (ppm)	Total Diluted Volume (ft^3)[b]	Sample Conc. (ppm)	Calc. Amt. of SO_2 Recovered (ppm)[a]	Percent Recovery
1	0.89	298	26.612	472	9239	1.37	1.36	101
2	0.89	298	26.612	472	9239	1.38	1.36	102
3	0.89	298	26.612	472	9239	1.36	1.36	100
							Average =	101%

---

[a] This concentration, representing 100% recovery, was obtained by back calculating from recovered sample concentration and percent recovery.

[b] Volume corrected to 1 atm pressure and 68°F.

TABLE 17. SULFUR DIOXIDE RECOVERY FROM DILUTE EXHAUST BY DIRECT CVS INJECTION DURING THE HOT FTP DRIVING CYCLE

	Nominal Flowrate (ft^3/min)		SO_2 Injected		SO_2 Recovered			
Test	SO_2	CVS	Vol. SO_2 Injected (ft^3)[b]	Conc. SO_2 Injected (ppm)	Total Diluted Volume (ft^3)[b]	Sample Conc. (ppm)[c]	Calc. Amt. of SO_2 Recovered (ppm)[a]	Percent Recovery
1	0.87	299	19.773	472	6886	1.35	1.36	99.6
2	0.87	299	19.773	472	6886	1.35	1.36	99.6
3	0.90	299	20.226	472	6869	1.34	1.39	96.4
4	0.90	299	20.226	472	6869	1.42	1.39	102
5	0.90	299	20.226	472	6869	1.41	1.40	101
							Average =	99.7%

---

[a] This concentration, representing 100% recovery, was obtained by back calculating from recovered sample concentration and percent recovery.

[b] Volume corrected to 1 atm pressure and 68°F.

[c] Includes baseline correction.

and it was found that sulfuric acid standards remained stable for at least fourteen weeks and the exhaust samples for at least two weeks but less than ten weeks. The actual lifetime probably lies between four and six weeks. This relatively long period of sample stability allows for some leeway in case the samples can not be analyzed immediately. The best collection efficiency was obtained when the dilute exhaust flowed at 4 ℓ/min through two bubblers in series, each containing 25 mℓ of 3 percent hydrogen peroxide maintained at ice bath temperature (0-5°C). Fluoropore filters (0.5 micron) are inserted in the sampling line each day to prevent contamination of the samples and subsequent column poisoning in the ion chromatograph. A possible 1-4 percent loss in sulfur dioxide recovery may be expected as a result of the filter. The loss might also be due to the filter trapping sulfuric acid from the exhaust and, thus, excluding it from the sample. The linearity of response of the ion chromatograph is maintained in the sulfate concentration range 0.5 to 100 $\frac{\mu g\ SO_4^{-2}}{m\ell}$ (100 ppm). However, changing the attenuation on the ion chromatograph causes a discontinuity in the calibration curve. This discontinuity is seen as a slope change in Table 14. The standards analyzed at each attenuation obviously fall into a linear pattern even though the slopes differ. A different set of standards must therefore be run for each sensitivity setting.

The results of the qualification tests indicate that 100 percent SO_2 is recovered from both the injection of sulfur dioxide into the CVS alone and the injection into dilute exhaust. The baseline SO_2 emission from the test car averaged at 0.49 ppm sulfur dioxide while the car was run on the hot FTP driving cycle.

The ion chromatographic method of sulfur dioxide analysis is a simple, sensitive, specific, and relatively rapid procedure with few interferences. No intermediate steps are involved, lessening the change of sample loss or contamination. The ion chromatograph is sensitive to 0.01 ppm SO_2 and samples can be analyzed in 10 to 15 minutes. The difference in retention times between the various ions in the sample allows for definite peak identification. Sulfate analysis on the ion chromatograph is also unaffected by most interferences plaguing a number of other sulfur dioxide procedures.

SECTION 5

NITROUS OXIDE PROCEDURE

LITERATURE SEARCH

There are six common oxides of nitrogen: nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), dinitrogen trioxide (N_2O_3), dinitrogen tetraoxide (N_2O_4), and dinitrogen pentoxide (N_2O_5). In addition to these, there are two different oxides that have the empirical formula NO_3. Both are very reactive and have only been identified by spectroscopy as transient species.

Nitrous oxide is a colorless, nonflammable gas at room temperature with a slightly sweet taste and odor. Some synonyms are dinitrogen oxide or nitrogen monoxide, hyponitrous acid anhydride, factitious air and laughing gas. Nitrous oxide is the least reactive and noxious of the oxides of nitrogen. At room temperature it is relatively inert; but at 500°C, it decomposes to nitrogen, oxygen, and nitric oxide and at elevated temperatures, it will support combustion and oxidizes certain organic compounds and alkali metals. Nitrous oxide, N_2O, has a molecular weight of 44.01, a melting point of -90.8°C, and a boiling point of -88.5°C. It is a linear molecule with a N-N bond distance of 1.128 Å and a N-O bond distance of 11.84 Å and is isoelectronic with carbon dioxide. When inhaled, nitrous oxide may cause hysteria, insensibility to pain, or unconsciousness and therefore used as an anesthetic for minor operations, including dentistry. It is also used as a nontoxic dispersing agent in commercial whipped cream. Commercially, nitrous oxide is prepared by the thermal decomposition of ammonium nitrate, the controlled reduction of nitrites or nitrates, the slow decomposition of hyponitrites, and by the thermal decomposition of hydroxylamine.

The analysis of nitrous oxide has been conducted using mass spectrometry, infrared spectroscopy, and gas chromatography. Of these, the most sensitive method is gas chromatography.

There are three gas chromatography methods that have been used to analyze for nitrous oxide. Two of these require cold traps to collect and concentrate the sample. With the third technique, grap samples are collected in Tedlar plastic bags and analyzed with an electron capture detector.

PROCEDURAL DEVELOPMENT

The gas chromatograph operating conditions and sampling system specifications were obtained from the Project Officer. A two column system with column backflush and isothermal termperature operation was constructed for the analysis. The stripper column is a 2' x 1/8" stainless steel tube filled with 10 percent OV-17 on 80/100 mesh Gas Chrom Q. The analytical column consists of a 6' × 18" stainless steel column packed with 120/150 mesh Porapak Q. A series of six port valves and timers is used to direct the sample flow through the columns. The samples are then analyzed with an electron capture detector. Since this method has been successfully applied to automotive exhaust, no other significant effort was applied to the procedural development. A description of the analytical system and the adapted procedure is presented as an appendix to this report.

VALIDATION EXPERIMENTS

Several experiments were conducted to validate the system for detector linearity, injection repeatability, and bag sample stability. Also, a means of calibrating the system using permeation tubes and calibration gases was investigated. The results are reported below.

Initially, a Tracor Model 412 Permeation System with an Ecocal permeation assembly was used to calibrate the instrument. The concentration of nitrous oxide could be set by changing the diluent gas flow over the permeation tube. This means of calibration can be used between the dynamic concentration range of 0.23 ppm to 6.31 ppm. However, a ghost peak was also generated with this permeation system. Efforts to eliminate this extraneous peak were unsuccessful. The permeation rate from this tube is not solely dependent on the concentration of nitrous oxide and would make this means of calibration difficult. Because of the problems associated with the permeation system, a static method of calibration was pursued. Four cylinders of calibration gas were obtained. The nitrous oxide concentrations of the cylinders ranged from 1.31 ppm to 9.90 ppm. No ghost peaks were observed and quantitative results were obtained.

Detector linearity over a wide range of concentrations is helpful and sometimes necessary when a variety of widely differing samples are to be analyzed. Such is the case with gaseous bag samples. No easy method to dilute the bag concentrations into the linear range of the instrument is available. Therefore, the detector must be linear in all of the concentration ranges expected. The detector linearity for the electron capture detector was determined with calibration gases from 1 to 10 ppm (Figure 17). Sample concentrations within this range are linear with respect to the detector.

With a gas sample loop and electrical/pneumatic sample flow control, sample injections are not as subject to human error and are more reproducible than syringe sample injections. The injection repeatability for the four calibration gas standards is shown in Table 18. This table demonstrates that sample injection reproducibility is reliable with the present analytical system.

Due to the length of time required for sample collection and subsequent gas chromatograph analysis, nitrous oxide must be stable for at least several hours. The bag stability was determined by taking a random Tedlar bag filled with exhaust from an emissions test. The two samples were reprocessed periodically. The first bag was processed hourly for five hours and the second bag was processed periodically for several weeks. The time sample decay curve for both samples is shown in Figures 18 and 19. Samples may be stored for a period of about two weeks without adverse effects to the sample concentration. After this time, it is difficult to preserve sample integrity.

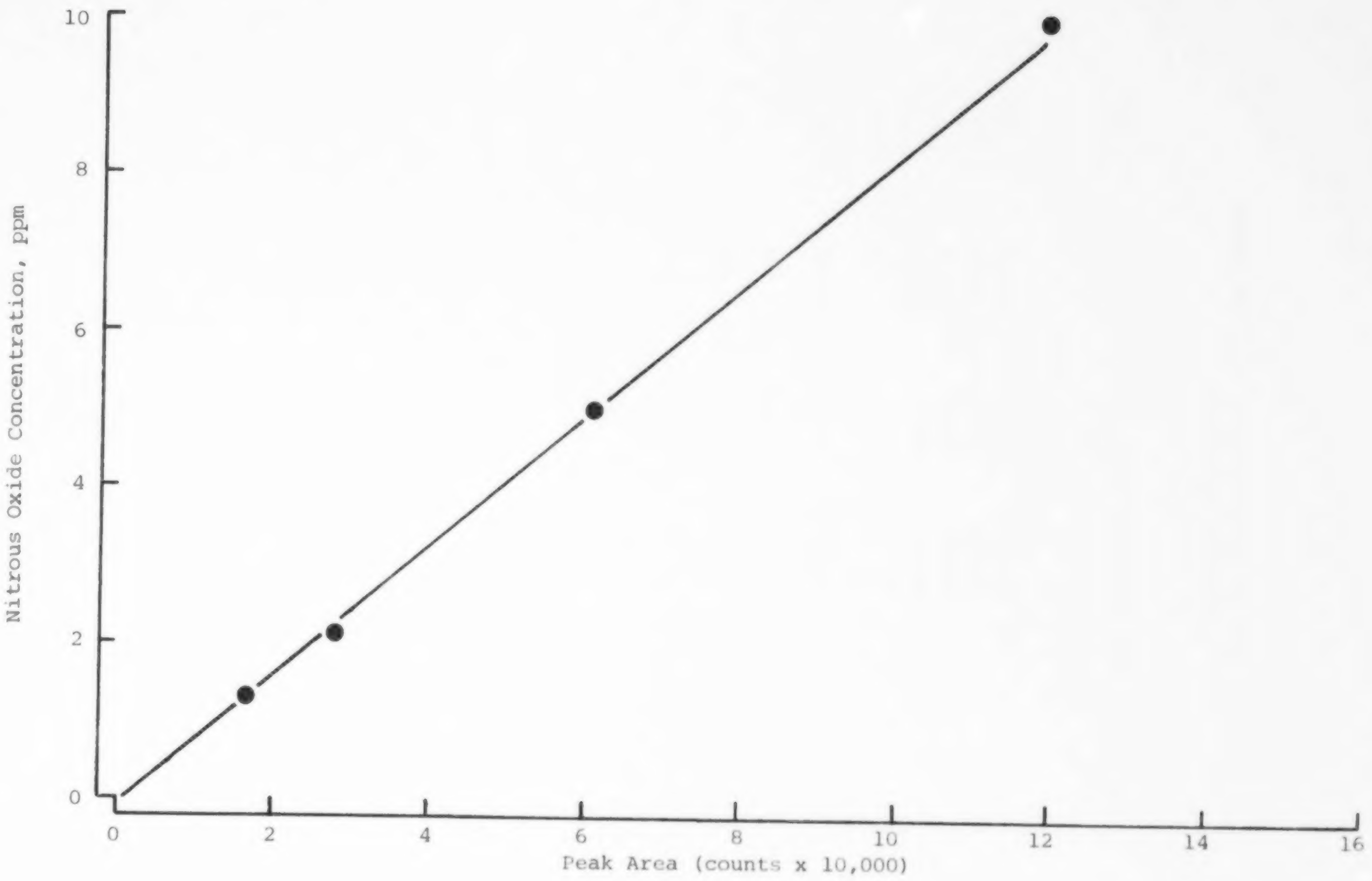

Figure 17. Detector linearity curve.

TABLE 18. INJECTION REPEATABILITY OVER THE RANGE OF DETECTOR LINEARITY

	N_2O Concentration, ppm			
	1.31	2.16	4.95	9.90
	Area			
	17935	28020	61146	118085
	17811	28759	61057	118935
	18346	28974	61004	118687
	18149	28931	61325	119448
	18319		61448	119810
				119005
Average	18112	28671	61196	118995
Standard Deviation	235	444	186	599
Coefficient of Variation	1.30	1.55	0.30	0.50

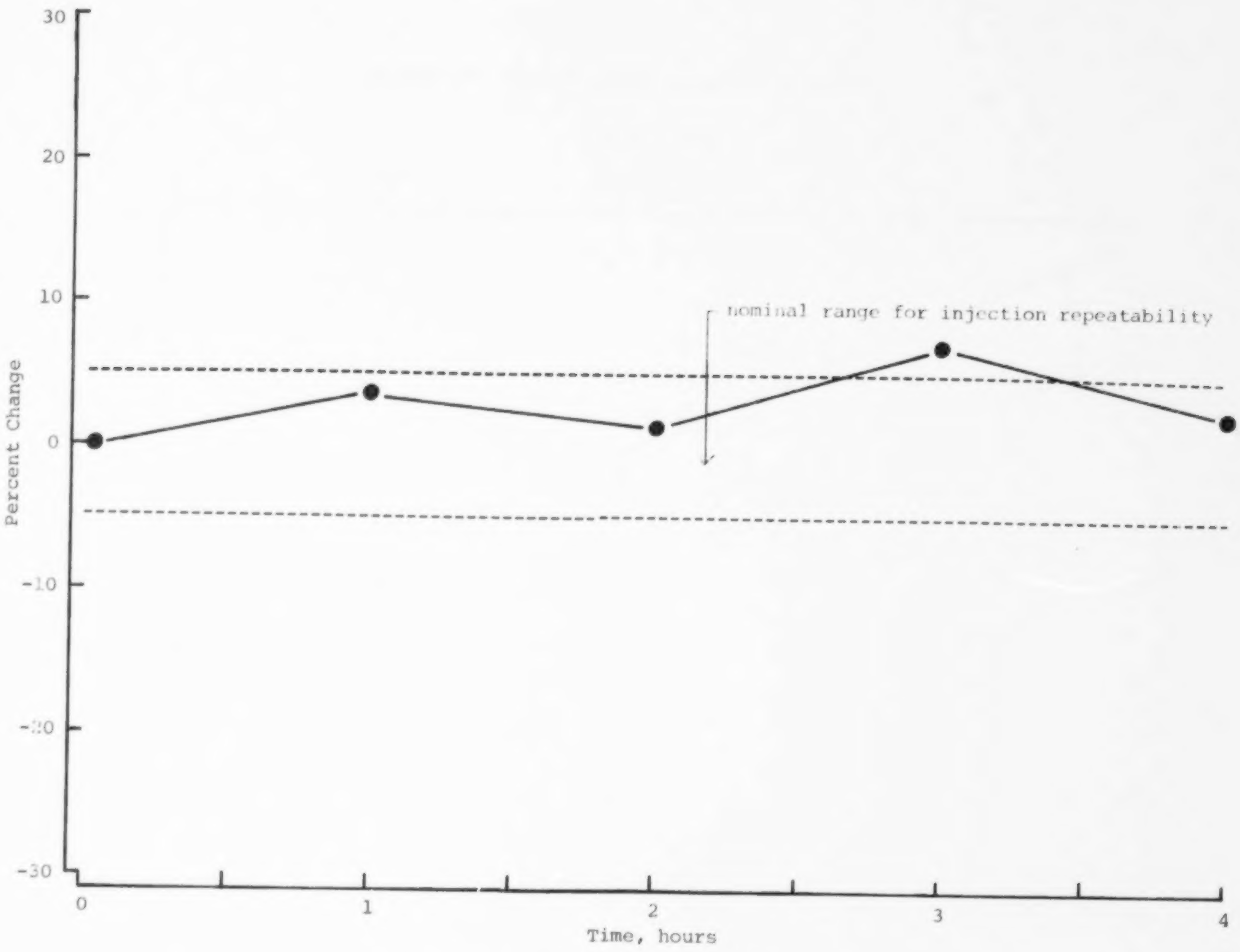

Figure 18. Sample decay curve (short term).

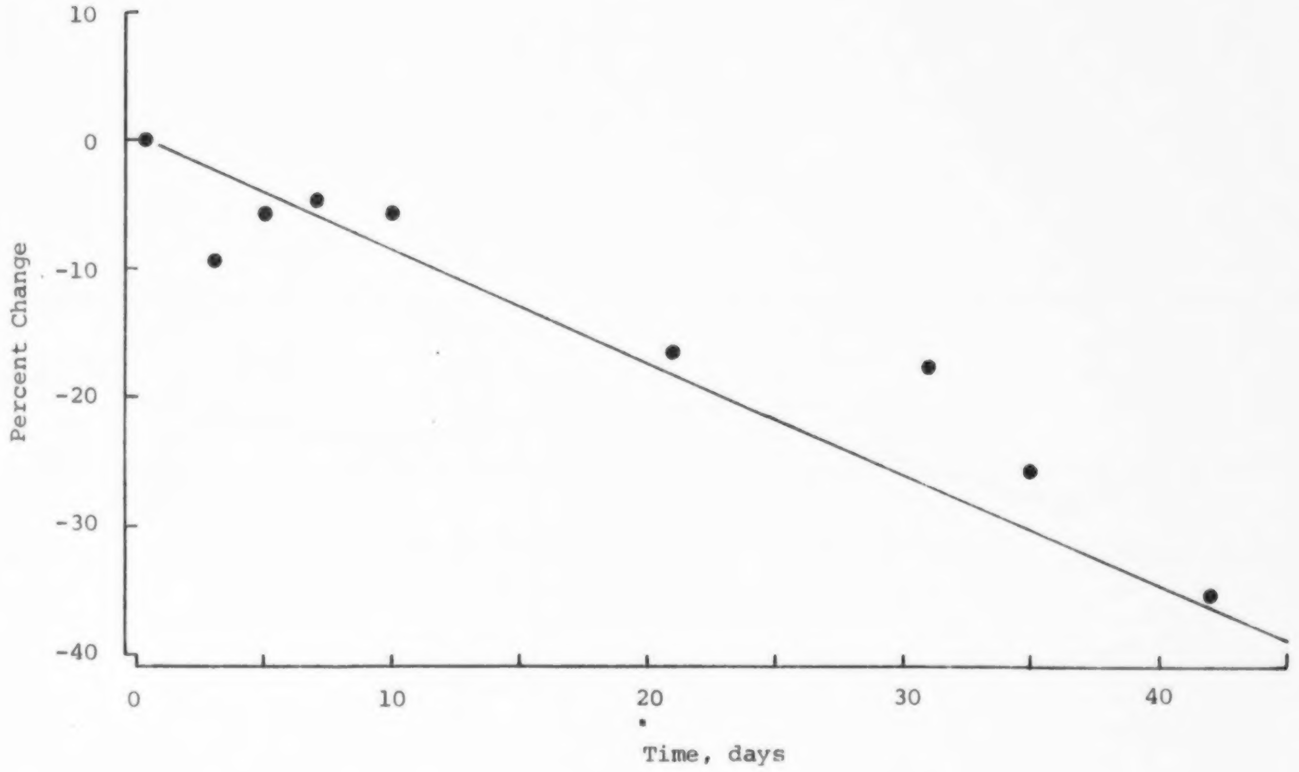

Figure 19. Sample decay curve (long term).

QUALIFICATION EXPERIMENTS

Qualification recovery experiments were conducted for nitrous oxide with two vehicles over several driving cycles and with several concentrations of nitrous oxide injected into the system. The three driving cycles employed in these experiments were the Federal Test Procedure (FTP), Sulfate Emissions Test, Cycle 7 (SET-7), and the Highway Fuel Economy Test (HFET). The vehicles tested were two Oldsmobile Cutlass Supremes with oxidation catalysts. The first was a 1977 model with a 260 V8 engine and the second was a 1978 model with a 305 V8 engine. Three concentrations of nitrous oxide were used to generate dilute concentrations ranging from 0.20 ppm to 7.19 ppm.

The baseline emission rates for each car were determined for the three driving cycles. These values are shown in Table 19. These baseline exhaust emission values were used to correct the observed concentrations with exhaust. These values were also corrected for the concentration of nitrous oxide in the air. The injection recoveries for the two vehicles are presented in Tables 20 and 21. The injection recoveries were also determined without the vehicle. Table 22 lists the results from these tests.

The combined recoveries over the four concentration ranges is essentially 100 percent. With each vehicle, the average percent recovery for the three different driving cycles is also 100 percent. Therefore, total sample recovery can be expected for the analysis and complete sample integrity is preserved in the CVS.

RESULTS AND CONCLUSIONS

The measurement of nitrous oxide in dilute exhaust can be conducted with a gas chromatography technique. Dilute exhaust is collected in a Tedlar bag as a grab sample. Sample analysis of the bag sample with an electron capture detector and comparison to a set of calibration blends determines the concentration in dilute exhaust. The minimum detectable limit of this procedure is 0.01 ppm.

Detector linearity, injection repeatability, bag sample stability, and a static means of calibration were demonstrated for the system. The electron capture detector employed is linear over the range of sample concentrations expected. This enables direct sample analysis without secondary dilution. The injection repeatability for an automated sampling system with a gas sampling loop is excellent for the analytical procedure. The sample integrity is also maintained if the samples cannot be analyzed immediately. This enables minor system repairs without holding up testing.

The average CVS percent recoveries is essentially 100 percent in dilute exhaust for nitrous oxide over the concentration ranges expected. No losses were observed with or without the vehicle. Even under a variety of emissions testing conditions (driving cycles and vehicle), the average percent recovery is consistent. This is expected due to the inertness and stability of nitrous oxide. Sample integrity can be expected throughout the entire testing procedure and sample concentrations are not subject to the instability of the compound tested.

TABLE 19. TYPICAL NITROUS OXIDE EXHAUST CONCENTRATIONS AND EMISSION RATES ON SEVERAL DRIVING CYCLES WITH TWO VEHICLES USED DURING QUALIFICATION EXPERIMENTS

Driving Cycle	Run	Bag	1977 260 V8 Olds Cutlass		1977 305 V8 Olds Cutlass	
			ppm N_2O[a]	mg/km[b]	ppm N_2O[a]	mg/km[b]
FTP (cold)	1	1	1.33	29.2	0.52	14.5
		2	0.42		0.27	
		3	1.68		0.77	
FTP (cold)	2	1	----	----	0.58	15.3
		2	----		0.25	
		3	----		0.86	
FTP (hot)	3	1	1.24	38.9	0.59	13.7
		2	0.68		0.23	
		3	2.36		0.72	
FTP (hot)	4	1	1.09	26.6	0.57	14.4
		2	0.46		0.18	
		3	1.41		0.99	
SET-7	5	only	1.26	24.6	0.98	19.2
SET-7	6	only	1.26	24.6	0.91	17.9
SET-7	7	only	1.40	27.5	0.98	19.3
		Avg	1.31	25.6	0.96	18.8
HFET	8	only	0.77	10.8	1.23	17.4
HFET	9	only	0.68	9.5	0.96	13.6
HFET	10	only	0.47	6.7	1.20	17.0
		Avg	0.64	9.0	1.13	16.0

(a) N_2O values are background corrected

(b) FTP emission rates are weighted

TABLE 20. NITROUS OXIDE INJECTION RECOVERIES WITH 1977 260 V8 OLDSMOBILE CUTLASS WITH OXIDATION CATALYST

Driving Cycle	Run	Nitrous Oxide, ppm: Calculated Amount Injected	Nitrous Oxide, ppm: Observed (Exhaust + Air + Injected)	Nitrous Oxide, ppm: Exhaust Only	Nitrous Oxide, ppm: Background	Percent Recovery
FET	1	7.04	8.88	0.64	0.37	111.8
FET	2	7.22	9.10	0.64	0.37	112.1
FET	3	7.41	9.21	0.64	0.37	110.6
SET-7	4	8.11	10.18	1.31	0.36	105.0

TABLE 21. NITROUS OXIDE INJECTION RECOVERIES WITH 1978 305 V8 OLDSMOBILE CUTLASS WITH OXIDATION CATALYST

Driving Cycle	Run	Nitrous Oxide, ppm: Calculated Amount Injected	Nitrous Oxide, ppm: Observed (Exhaust + Air + Injected)	Nitrous Oxide, ppm: Exhaust Only	Nitrous Oxide, ppm: Background	Percent Recovery
FTPcs	1	8.73	8.85	0.55	0.33	91.3
FTPs	1	8.80	9.73	0.26	0.33	103.8
FTPhs	1	8.89	10.12	0.82	0.33	100.9
FTPcs	2	8.35	9.21	0.55	0.40	98.9
FTPs	2	8.59	9.83	0.26	0.40	106.7
FTPhs	2	7.88	11.24	0.82	0.40	116.4
FET	3	9.24	11.58	1.13	0.33	109.6
SET-7	4	9.28	11.72	0.96	0.33	112.4

TABLE 22. NITROUS OXIDE CVS QUALIFICATION EXPERIMENTS - NO VEHICLE

Injection Blend Concentration, ppm N_2O	Nominal Flow Rate, ft^3/min		Calculated ppm N_2O Dilute[a]	Run	Observed ppm N_2O[a]	Percent Recovery
	N_2O Blend	CVS				
95	0.75	350	0.23	1	0.27	118.7
95	0.75	350	0.22	2	0.26	115.9
				Avg	0.27	117.3
831	0.40	350	0.80	1	0.96	119.5
831	0.40	350	0.77	2	0.64	83.7
				Avg	0.80	101.6
831	0.75	350	1.97	1	1.98	100.5
831	0.75	350	2.03	2	2.28	112.5
			2.00	3	2.28	114.0
				Avg	2.18	109.0
8075	0.35	350	6.64	1	6.90	103.9
8075	0.35	350	6.27	2	7.12	110.0
				Avg	7.01	107.0

This procedure provides a rapid and sensitive method for the analysis of nitrous oxide in dilute exhaust. A single bag sample requires about two minutes for sample loop purging and seven minutes for the automated analysis. The total analysis time is about nine minutes per sample. The automated system provides simplicity and ease of operation and makes this procedure ideal for routine analysis.

SECTION 6

INDIVIDUAL HYDROCARBON PROCEDURE

LITERATURE SEARCH

The eight individual hydrocarbons (methane, ethane, ethylene, acetylene, propane, propylene, benzene, and toluene) have been measured by innumerable techniques. One of the most efficient techniques for the individual determination of all of these compounds in a single analysis is with gas chromatography. Because of its efficiency, this means of analysis was selected over any of the other available.

Hydrocarbons are of interest as exhaust components because of their potential for photochemical smog formation. Hydrocarbons are palced into four classes according to their participation in atmospheric reactions. Methane, ethane, acetylene, propane, and benzene are placed in the Class I, the nonreactive category. The Class II reactive category includes the C_4 and higher paraffins, while the Class III reactive category encompasses all of the aromatics except benzene. The olefins are placed in the Class IV reactive category. When olefins such as ethylene react with ozone

$$O_3 + H_2C + HC_2 \rightarrow H_2C = O + H\dot{O} + H\dot{C}O$$

the precursors of photochemical smog are formed. These free radicals then participate in other atmospheric reactions that result in oxidant formation.

Dimitriades and Seizinger(73) proposed a three-column system capable of analyzing at least 22 hydrocarbons. Two packed columns were required to resolve the C_1 and C_2 hydrocarbon components and an open tubular column was used to resolve the other components. The complete analysis consisted of two different sample loop sizes. This procedure was considered time consuming and the number of compounds to be analyzed was excessive for the project.

Papa et al(74) presented a procedure for the analysis of C_1 and C_{12} hydrocarbons in automotive exhaust. This dual column system consisted of a packed column with a mixture of stationary phases for the resolution of C_1 and C_2 hydrocarbons and an open tubular column. About 200 individual peaks were obtained from the method. This procedure also required two sample loop injections. Excessively low temperatures were required for resolution of C_1 and C_2 hydrocarbons with this analytical system.

Klosterman and Sigsby(75) proposed a simple analytical system for the determination of hydrocarbons according to their potential for photochemical smog formation. A flame ionization analyzer was used in their work, though this technique did not employ the use of a gas chromatograph. A column similar to that used by Klosterman and Sigsby was used to scrub the oxygenated hydrocarbons and olefins from benzene and toluene by Black et al(76). This method utilizes four packed analytical columns for the resolution of the desired compounds. Methane, ethane, ethylene, acetylene, propane, and propylene are resolved with the first two columns; and benzene and toluene are resolved with the other two. As with the other procedures, two sample loops are required for the combined analysis of paraffins, olefins, and aromatic hydrocarbons. This procedure was also designed as a simple and inexpensive method for the determination of smog related compounds. Table 23 lists the compounds of interest, along with chemical formulas, boiling and melting points, synonyms, and molecular weights.

PROCEDURAL DEVELOPMENT

The gas chromatographic procedure for the determination of the individual hydrocarbons in dilute exhaust is currently "in hand" and has been used on a variety of projects. The four column system is capable of resolving the eight individual hydrocarbons. Columns I and II in the system consist of an 8' x 18" stainless steel tube packed with 80/100 mesh Porapak Q and a 4' x 1/8" teflon column packed with 35/60 mesh type 58 silica gel, respectively. Column III consists of a 15' x 1/8" stainless steel tube packed with 15 percent, 1, 2, 3-tris(2-cyanoethoxy)propane on 60/80 mesh chromosorb PAW; and column IV consists of a 2' x 1/8" stainless steel tube packed with 40 percent mercury sulfate ($hgSO_4$) and 20 percent sulfuric acid (H_2SO_4) on chromosorb W. Columns II, III, and IV are used isothermally and column I undergoes a temperature program sequence. The primary purpose of Column I is to resolve methane from air, while Column II resolves C_2 and C_3 hydrocarbons. Columns III and IV resolve benzene and toluene from the other aromatics, paraffins, olefins, acetylenes, and oxygenated hydrocarbons. Three timers, four solenoid valves, and five si-port gas sampling valves are required to accomplish the complicated sample flow through the columns. No procedural development was required for this analysis. The actual analytical procedure is included as an attachment to this report.

VALIDATION

Since this gas chromatographic procedure has been used with much success on a variety of projects, procedural validation was limited to injection repeatability and bag sample stability experiments. These were determined during routine analysis and demonstrate the stability of the instrumentation. All other parameters were determined from previous experience with this analytical procedure.

The injection repeatability for the individual hydrocarbon procedure was conducted on two separate occasions. Table 24 shows the data accumulated on each occasion. The injection repeatability for the two 10 ml sample loops is not greater than ± 2 percent.

The bag sample stability experiment was conducted on a random sample from an emissions test. The sample was collected during the driving cycle and analyzed immediately afterward. This sample was then reprocessed periodically for several weeks. A bag sample of the calibration standard and a bag sample

TABLE 23. IMPORTANT FACTS ON INDIVIDUAL HYDROCARBONS

Compound	Formula	Molecular Weight	Melting Point	Boiling Point	Synonyms
Methane	CH_4	16.04	-182.48	-164	marsh gas, methyl hydride
Ethylene	C_2H_4	28.05	-169.15	-103.71	ethene, elayl, olefiant gas
Ethane	C_2H_6	30.07	-183.3	- 88.63	bimethyl, dimethyl, methylethane, ethyl hydride
Acetylene	C_2H_2	26.04	- 80.8	- 75	ethyne, ethine
Propane	C_3H_8	41.11	-189.69	- 42.07	dimethylmethane, propyl hydride
Propylene	C_3H_6	42.08	-185.25	- 47.4	propene, methylethylene, methylethene
Benzene	C_6H_6	78.12	5.5	80.1	benzol, phene, cyclohexatriene
Toluene	C_7H_8	92.15	- 95	110.6	methylbenzene, phenylmethane, toluol, methacide

TABLE 24. INJECTION REPEATABILITY ON TWO SEPARATE OCCASIONS

	Methane	Ethylene	Ethane	Acetylene	Propane	Propylene	Benzene	Toluene
1	7283	10097	9597	12034	14809	15569	13697	15348
2	7527	10467	9873	12544	15092	15724	13815	15570
3	7792	10621	10039	12803	15352	16152	13877	15466
4	7566	10479	9892	12628	14825	15910	13977	
5	7585	10495	9900	12675	15016	15899	13824	15478
6	7387	10300	9690	12398	14925	15441	14041	15576
7	7700	10575	9994	12753	15147	15931	14042	15780
8	7455	10307	9724	12460	14702	15629	14066	15799
9	7680	10433	9878	12624	14933	15842	14049	15459
10	7618	10481	9885	12714	14996	15857	13943	15783
Average	7559.30	10431.50	9847.20	12563.30	14979.70	15795.40	13913.10	15584.33
Standard Deviation, S_x	152.98	154.55	136.90	224.85	187.42	206.83	125.33	166.20
Coefficient of variation, C_v	2.02	1.48	1.39	1.79	1.25	1.31	0.90	1.07
1	8593	11893	10973	14803	15705	17867	16466	18546
2	8633	11937	11011	14992	15912	18020	16604	18537
3	8602	11993	11067	15139	15722	17818	16553	18735
4	8640	11885	10977	15170	15775	17926	16409	18479
5	8702	12022	11113	15371	15825	17850	16267	18530
6	8561	11900	10946	15252	15879	17955	16433	18562
Average	8622	11938	11015	15121	15803	17906	16455	18565
Standard Deviation, S_x	48.59	57.20	63.70	200.07	83.77	75.10	118.21	87.95
Coefficient of variation, C_v	0.56	0.48	0.58	1.32	0.53	0.42	0.72	0.47

of exhaust doped with the calibration standard were also processed periodically. The time-sample decay curve for each compound is shown in Figures 20, 21, and 22. The sample integrity can be preserved for approximately five days.

QUALIFICATION EXPERIMENTS

The analysis of individual hydrocarbons in dilute exhaust has previously been conducted on many projects. On the request of the Project Officer, no qualification experiments were conducted with the CVS for this procedure. Also, long term experience with this procedure has given an insight into the sample integrity for the complete analytical system.

RESULTS AND CONCLUSIONS

The measurement of individual hydrocarbons in dilute exhaust has been conducted with a gas chromatography technique. Tedlar film bags are filled with dilute exhaust during each driving cycle. Analysis of the bag sample requires a complicated system of four analytical columns with backflush and temperature program capability. Sample concentrations are determined by comparison to a calibration blend of all eight hydrocarbons. The minimum detectable limit is 0.1 ppmC to 0.2 ppmC. The higher molecular weight compounds approach the higher minimum detectable limit.

Injection repeatability and bag sample stability were demonstrated for the system. The largest injection variability was with methane and acetylene and the smallest was with benzene and toluene. A 2 percent variability can therefore be expected for the six components of the first sample loop and first two columns (C_1 - C_3), and a 1 percent variability can be expected for the second sample loop and second two columns (benzene and toluene). This agreement is much better than can be expected of a syringe sample injection. The bag sample stability shows that dilute exhaust samples will be stable for about five days. Only propylene and toluene were shown to have a large decrease in concentration over a period of time in exhaust. With the standard only sample, all compounds showed the same decrease in concentration. A leak in the bag is suspected as a cause of this drastic change in concentration. However, even with a leak in the bag, the sample concentration is stable for about five days. Samples must be analyzed before this time to maintain confidence in the sample concentrations obtained. Otherwise, the sample integrity is lost due to sample decay, bag leakage, and/or permeation through the walls of the bag.

This procedure provides an effective means for the analysis of individual hydrocarbons in dilute exhaust. A single bag requires about four minutes to purge the sample loops, 23 minutes for total peak elution, and five minutes to cool the oven temperature back to room temperature and reset the instrumentation. The total analysis time per sample is about 32 minutes. The automated system provides a simplified operation for an otherwise complicated procedure and enables routine analysis for a large quantity of samples.

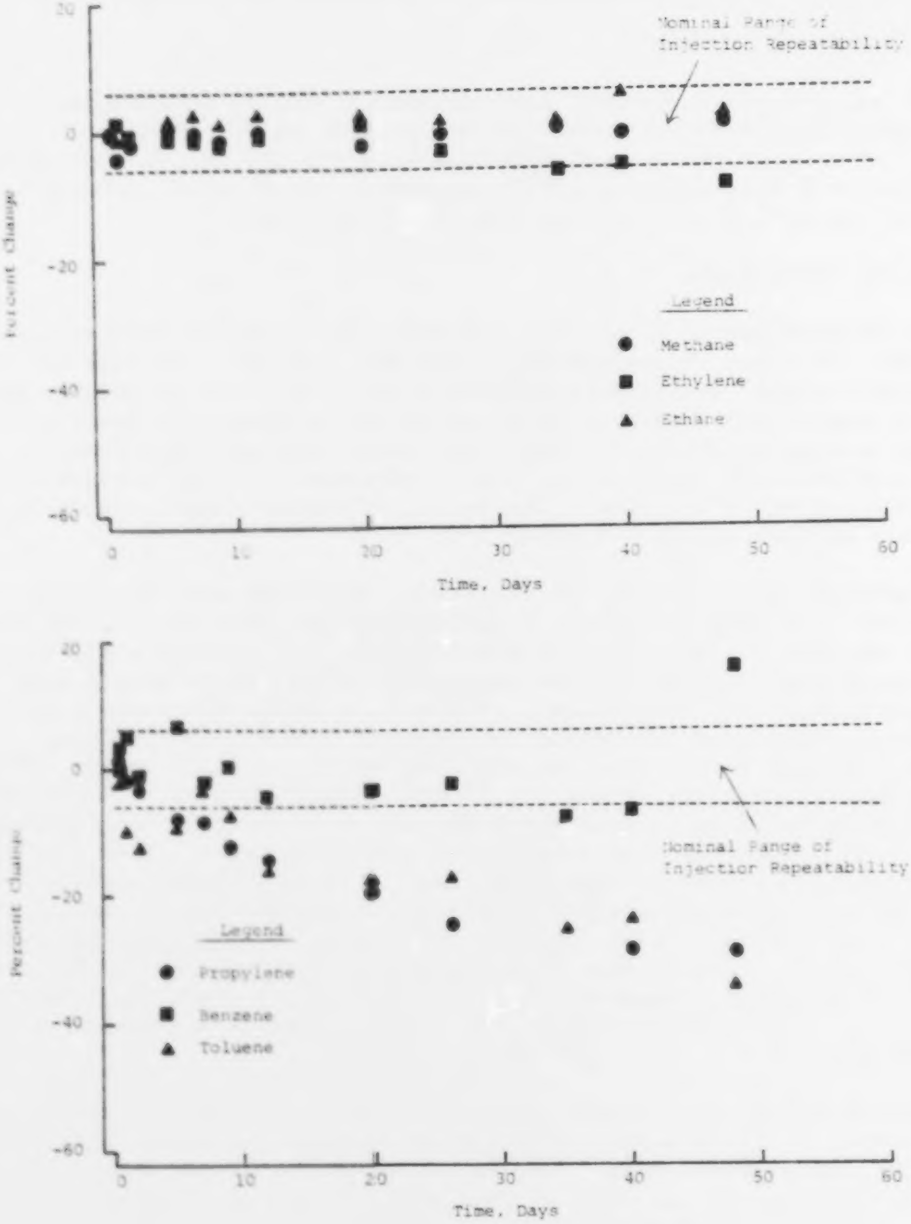

Figure 20. Time-sample decay curve (exhaust only).

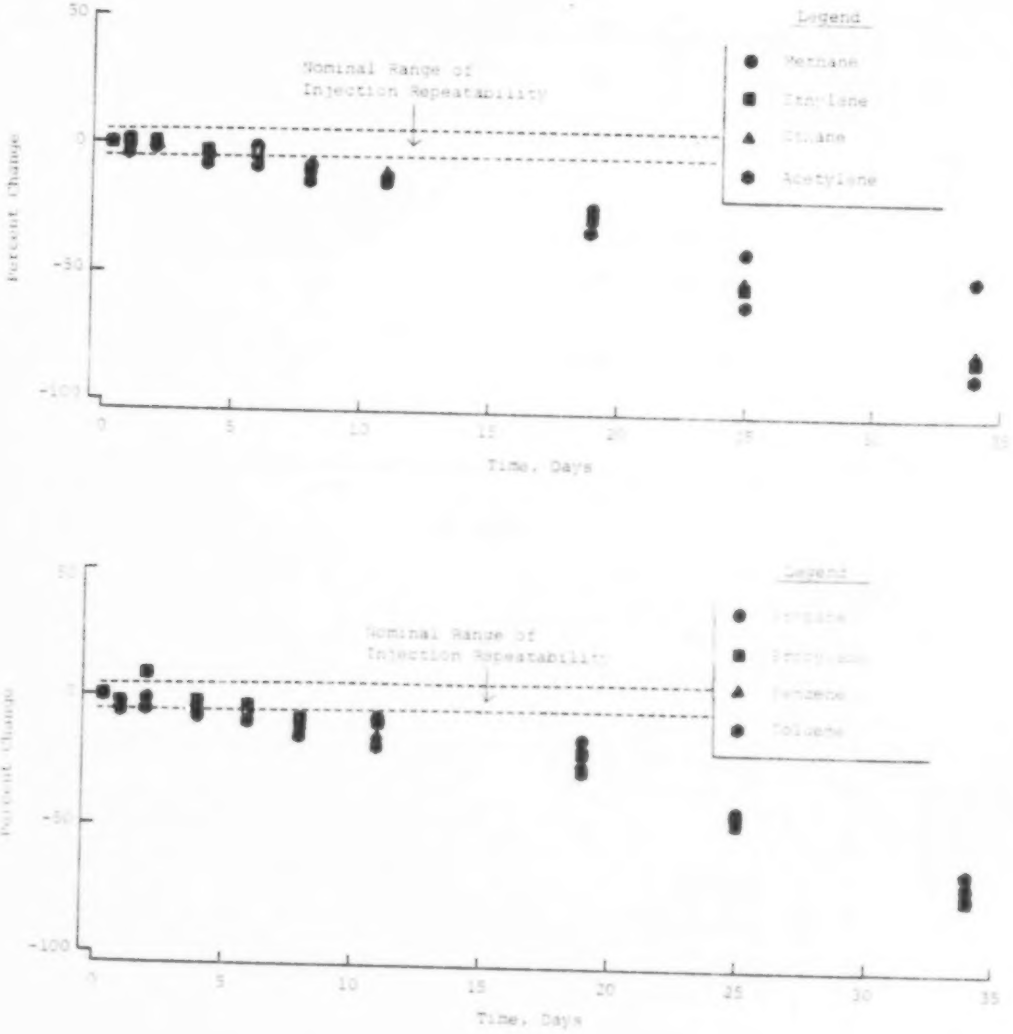

Figure 21. Time-sample decay curve (standard only).

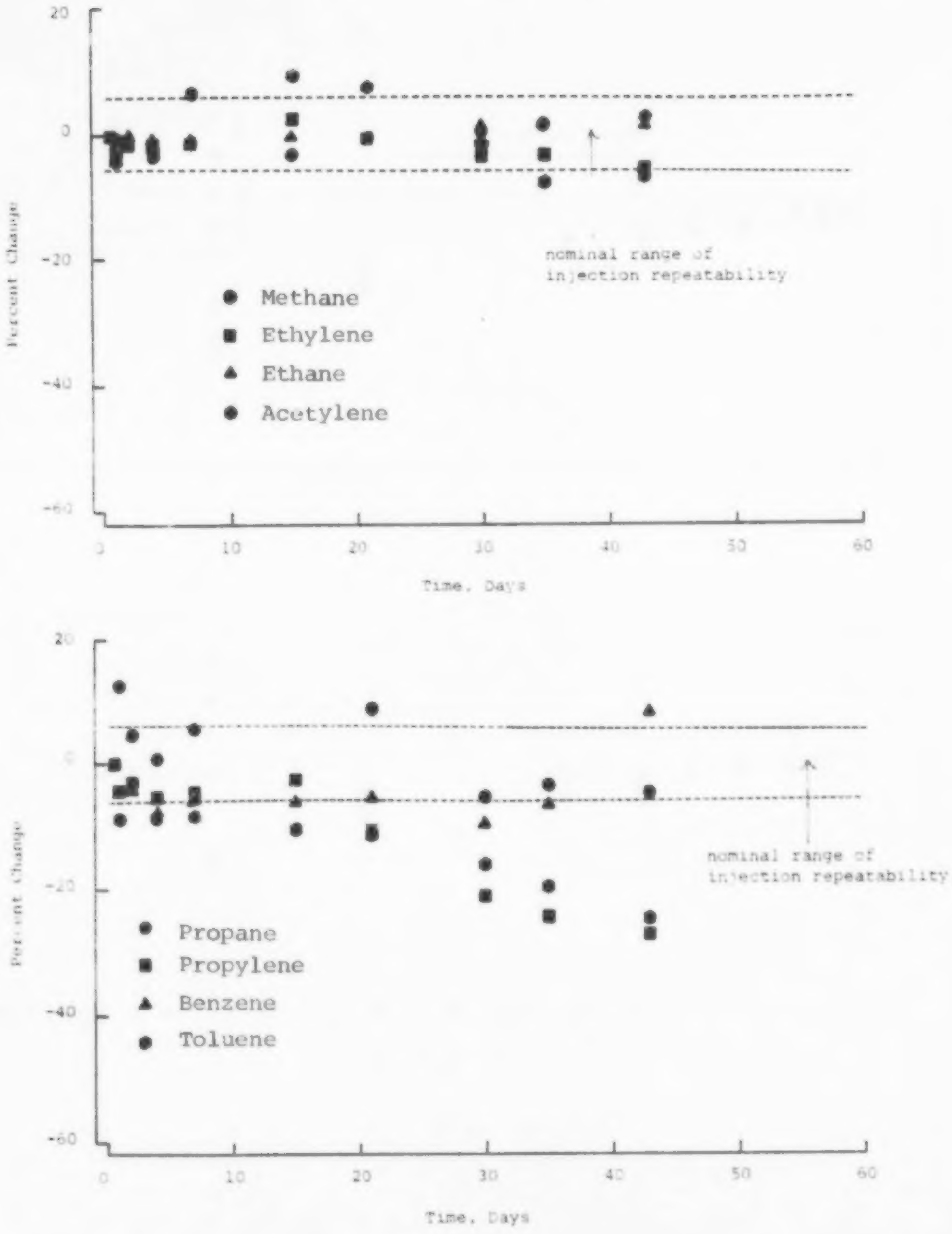

Figure 22. Time-sample decay curve (exhaust and standard).

SECTION 7

HYDROGEN SULFIDE PROCEDURE

LITERATURE SEARCH

Hydrogen sulfide is a very flammable and toxic gas at room temperature and has the characteristic odor of rotten eggs. The chemical formula for hydrogen sulfide (hydrosulfuric acid or sulfureted hydrogen) is H_2S. Hydrogen sulfide is a bent molecule with a H-S-H bond angle of 93.3° and an S-H bond distance of 1.3455 Å. Hydrogen sulfide has a boiling point of -60.33°C, a melting point of -85.49°C, and a molecular weight of 34.08. It is a very weak diprotic acid with dissociation constants:

$$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^- \qquad K_1 = 5.7 \times 10^{-8}$$

$$HS^- + H_2O \rightleftharpoons H_3O^+ + S^= \qquad K_2 = 1.2 \times 10^{-15}$$

Hydrogen sulfide may be detected by its odor at about 1 ppb; however, olfactory fatigue soon results and higher concentrations may not have an unduly objectionable odor. Death is caused by systemic poisoning and respiratory paralysis from exposure to high concentrations.

Hydrogen sulfide is prepared commercially as a by-product from many chemical processes and by the treatment of metallic sulfides with a mineral acid such as hydrochloric or sulfuric acid. Hydrogen sulfide produced in exhaust is probably formed by the reduction of sulfur compounds in the fuel. With an excess of oxygen, it burns to form sulfur dioxide and water:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

and with insufficient oxygen to form free sulfur and water:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

Hydrogen sulfide also reacts with sulfur dioxide to form free sulfur and water:

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

This reaction may be significant if high levels of sulfur dioxide are produced in exhaust.

The analysis of hydrogen sulfide has been conducted with an entire spectrum of analytical methods. Some of these methods include: surface reactions on plates, tiles, tapes or filters, wet chemical, fluorimetry, infrared spectroscopy, sulfur ion selective electrode, coulometry, gas chromatography, and colorimetry. Most of these are not applicable to dilute exhaust sampling but are applicable for ambient air sampling and "on line" systems. The best applicable means of analysis for dilute exhaust is the colorimetric technique.

There are two colorimetric methods available for the analysis of hydrogen sulfide. These are the sodium nitroprusside method and the methylene blue method. The sodium nitroprusside method has a lower detection limit of about 1 ppm. This method was not considered sensitive enough for the concentrations expected in dilute exhaust. The methylene blue method, on the other hand, has a reported lower detection limit of 1-3 ppb.

The absorbing reagent is the key to successful analysis with this procedure. Hydrogen sulfide is precipitated as the sulfide in the presence of metal ions. Cadmium and zinc hydroxide, cadmium sulfate, and zinc acetate have been used as the absorbing media. However, several authors have reported the oxidation of cadimium and the photochemical decomposition of cadmium sulfide. Bamesberger and Adams (77) suggested the use of 1 percent STRactan 10 as a stabilizer for cadmium absorbing solutions. On the other hand, zinc solutions do not appear to have these inherent problems. Flamm and James (78) tested all of the above absorbing reagents and found zinc acetate to be the most efficient absorbent. For these reasons, zinc acetate was selected as the best absorbing reagent.

PROCEDURAL DEVELOPMENT

A procedure for the analysis of hydrogen sulfide by the methylene blue method was obtained from the Project Officer under EPA Contract 68-03-2499. This procedure is a modification of the technique used by Gustafsson (79). A buffered zinc acetate solution is used as the absorbing reagent. This procedure was compared to the one recommended for ambient air sampling by Adams et al (80) which used cadmium hydroxide as the absorbing reagent. The selected analytical procedure is included as an attachment to the interim report.

The cadmium hydroxide method presented several problems. First, sulfides in alkaline solutions are easily oxidized by air. Second, cadmium sulfide is photosensitive and solutions must be protected at all times from exposure to light. The use of special glassware or aluminum foil wrappings are necessary to prevent exposure to light. The addition of a stabilizer such as STRactan 10 helps to minimize the effect of photochemical decomposition, but special handling precautions are still necessary. Because of these reasons, cadmium solutions are hard to work with, and some cadmium compounds are toxic. Cadmium, cadmium oxide, cadmium sulfate, and cadmium sulfide were included on a tentative carcinogen list issued by OSHA in July, 1978. Zinc sulfide, on the other hand, is not photosensitive, the solutions are much easier to work with, and zinc compounds are not as toxic. The problems with the cadmium hydroxide method were demonstrated by comparing the two methods.

Several authors have reported that methylene blue may be bleached by exposure to light. In order to determine what effect this might have on a developed sample, two high (18-19 µg/100 mℓ) and two low (2-3 µg/100 mℓ) concentration standards were prepared and developed for fifteen minutes. One of each concentration was then exposed to light. After developing for 15 minutes in the dark, the other two were wrapped with aluminum and stored in the dark. The absorbance of each was determined periodically for several weeks. The time-light exposure decay curves are shown in Figures 23 and 24. The results are discussed in the Results and Discussion Section.

Hydrogen sulfide is readily volatilized from acidic aqueous solutions. In alkaline solutions sulfide ion may be oxidized by dissolved oxygen. The pH of the buffered zinc acetate absorbing reagent is 7.0. This reagent remains at a pH of 7 even after bubbling with dilute exhaust. Oxidation of dissolved sulfide ion does not occur rapidly at this pH. After addition of the amine solution and ferric ion to the absorbing reagent, the pH is below 2.0. At this pH, the trapped sulfide ion reacts to form methylene blue. Buffering of the absorbing reagent and subsequent change of pH in the presence of the amine solution and ferric ion minimizes the losses due to oxidation or volatilization.

There are two possible methods available for generating a Beer's Law plot for calibration. The first technique requires extensive reagent preparation and tedious titrations. Thiosulfate solution is standardized against potassium dichromate. This standardized thiosulfate solution is used to standardize a dilute iodine solution. The standard sulfide solution concentration is then determined with an iodometric method. Aliquots of the standardized sulfide solution are used to generate a Beer's Law curve.

The other method requires the use of a hydrogen sulfide permeation tube. The calibration curve is generated by bubbling a known concentration of hydrogen sulfide for varying lengths of time. Generation of a calibration curve in this manner takes into account the collection efficiency of the bubblers. This method is quick, efficient and more consistent with the way the samples are actually taken. It also enables the generation of a daily calibration curve without being manpower intensive.

The calibration curve for methylene blue is shown in Figure 25. This curve was determined for a standardized sulfide ion solution on two separate occasions and follows Beer's Law at low concentrations. After about 70 µg$S^{=}$/100 mℓ, the curve begins to deviate from Beer's Law. Concentrations of hydrogen sulfide in dilute exhaust are expected to stay well within the linear range of the calibration curve.

VALIDATION EXPERIMENTS

After selecting an analytical method, validation experiments were conducted to determine the necessary sampling and procedural parameters. These experiments included trapping efficiency, calibration curve linearity, and interferences from dilute exhaust. Since the methylene blue procedure is a well documented analytical technique, only simple experiments were conducted to verify any other procedural parameters. Collection efficiency and

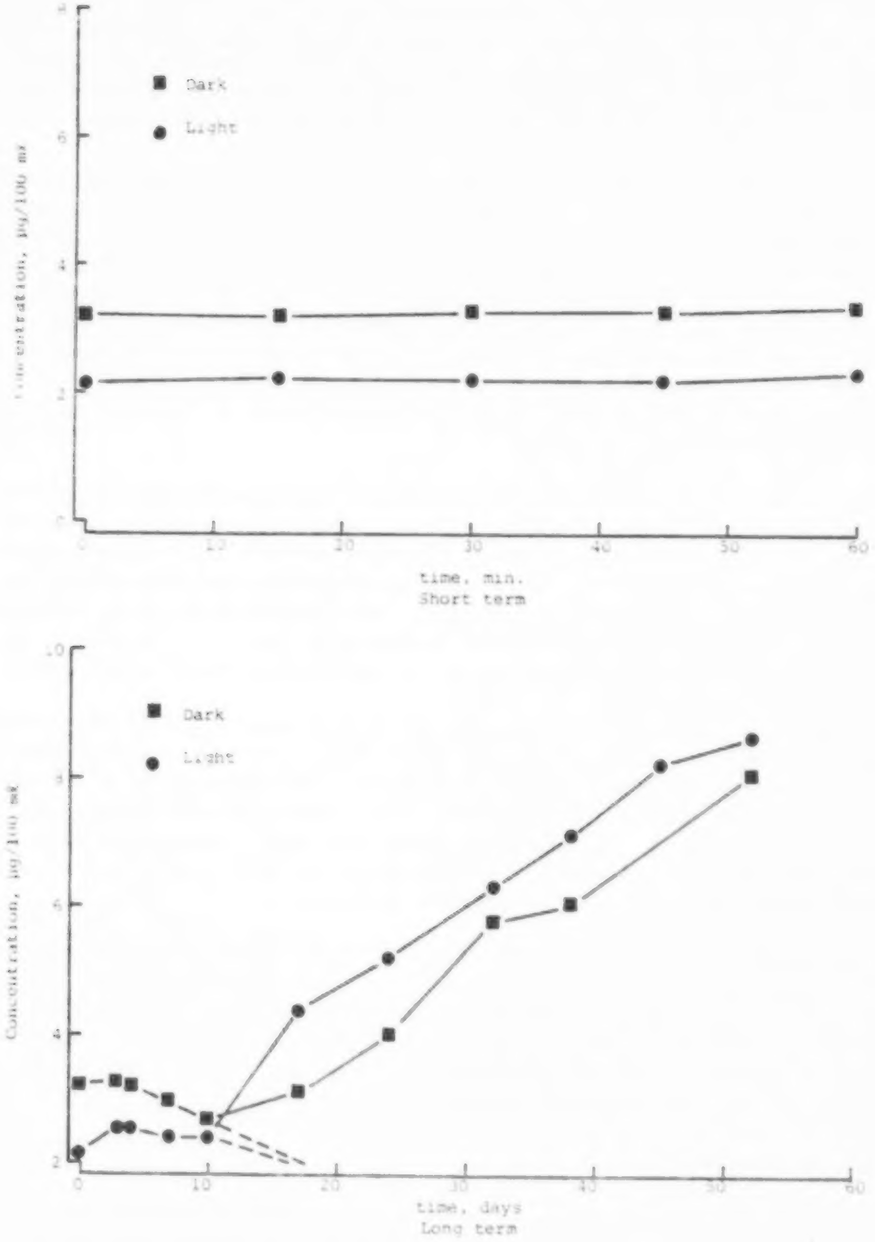

Figure 23. Time-Light exposure study (low concentration).

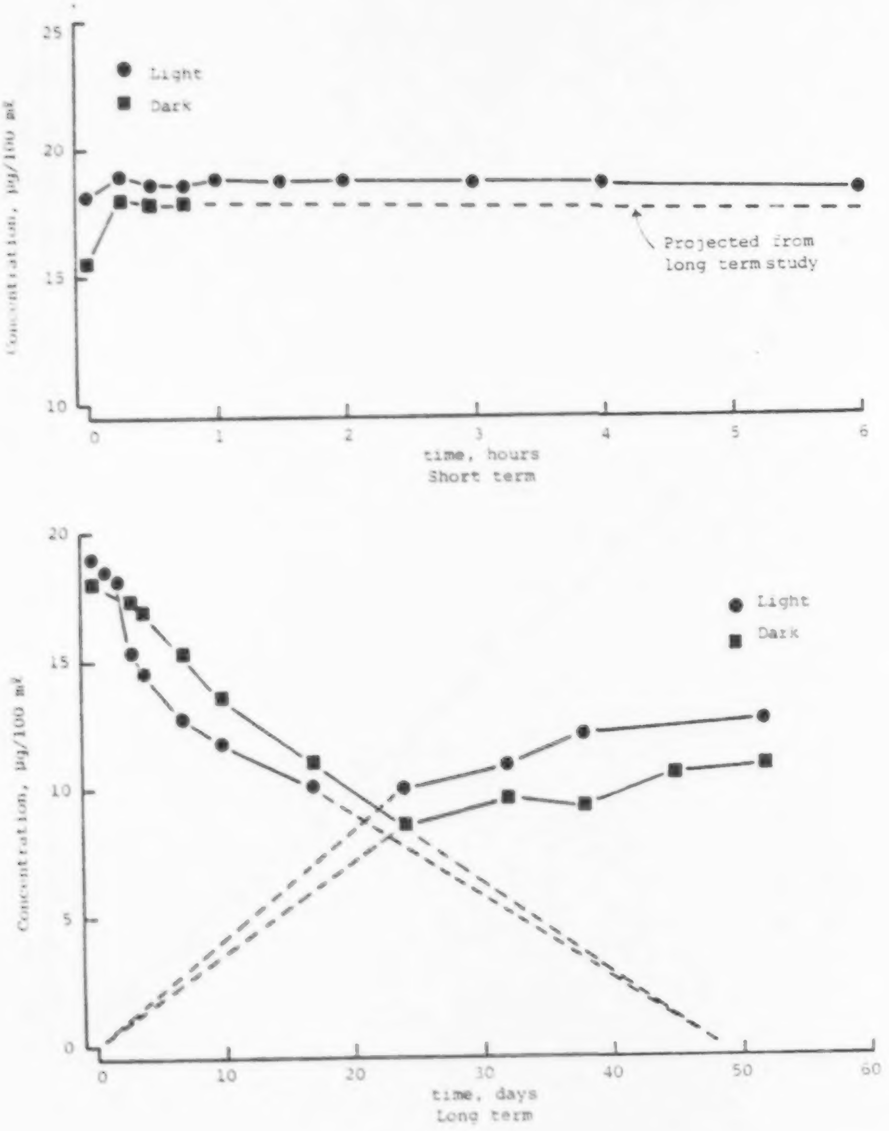

Figure 24. Time-Light exposure study (high concentration).

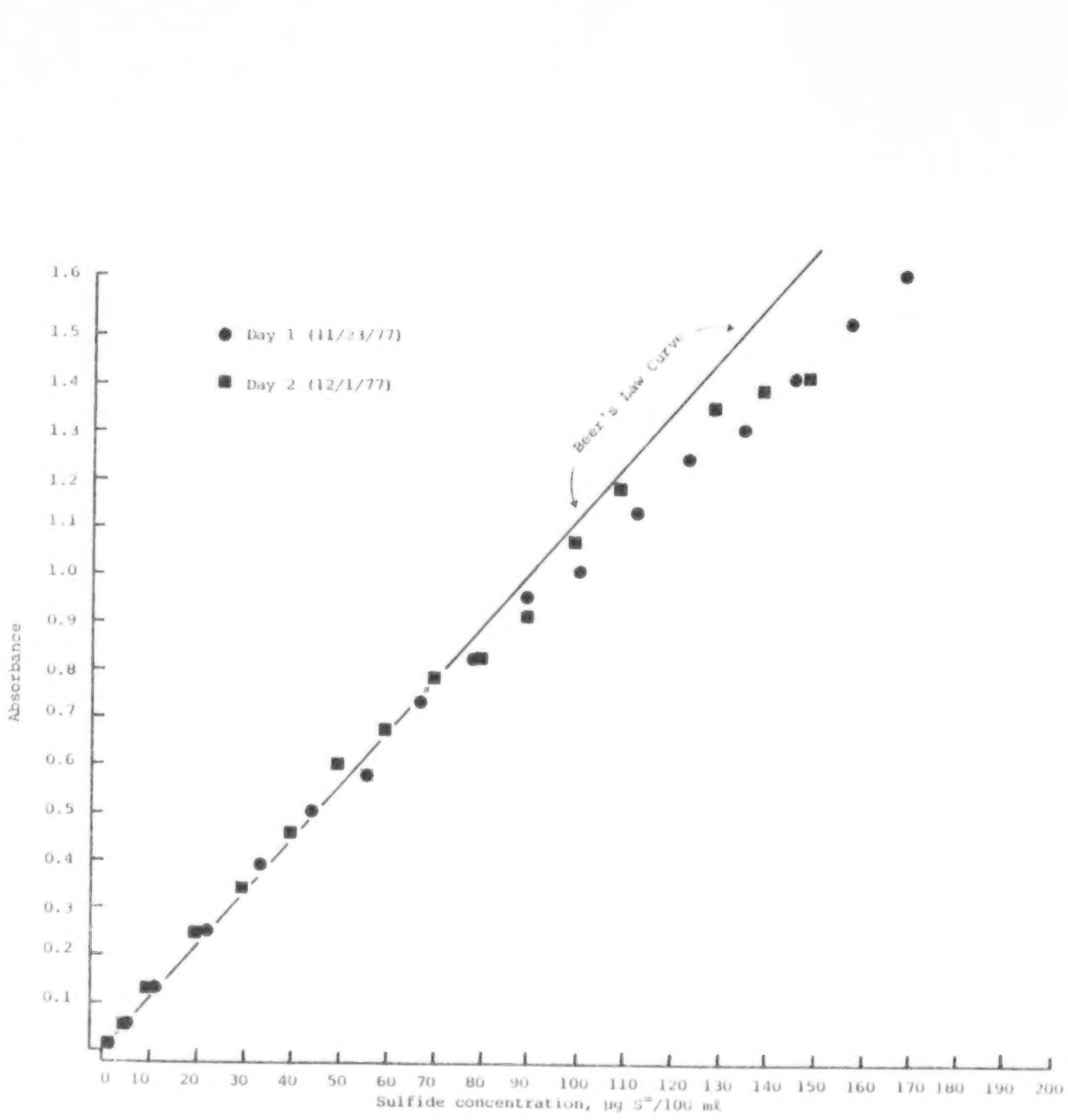

Figure 25. Beer's Law plot for methylene blue.

other sampling parameters were determined with a series of experiments. The first experiment determined the collection efficiency at room temperature (23° to 26°C). A 5 ppm concentration of hydrogen sulfide was passed through the absorbing reagent at 1.0 and 4.0 ℓ/min. The experiment was then repeated with a sample flow of 4.0 ℓ/min and an absorbing reagent temperature of 0° to 5°C. This temperature was achieved by immersing the impingers in an ice bath. The data for this study is shown in Table 25. Sample flow rate and absorbing reagent temperature did not have a measurable effect on the collection efficiency.

TABLE 25. THE EFFECT OF SAMPLE FLOW RATE AND ABSORBING REAGENT TEMPERATURE ON THE COLLECTION EFFICIENCY

Test Number	Absorbing Reagent Temp., °C	Sample Flow Rate	Percent H_2S Collected per Bubbler		
			1	2	3
1	23	1.0	98.0	1.7	0.3
2	23	1.0	98.2	1.3	0.5
		Avg.	98.1	1.5	0.4
1	25	4.0	96.4	3.2	0.4
2	25	4.0	96.4	3.0	0.5
3	25	4.0	95.7	3.8	0.5
4	25	4.0	95.9	2.5	1.6
		Avg.	96.1	3.1	0.8
1	0	4.0	95.0	5.0	---
2	0	4.0	93.9	5.3	0.8
3	0	4.0	92.8	6.2	0.9
4	0	4.0	92.7	6.3	0.9
		Avg.	93.6	5.7	0.9

The interferences for this procedure are also well documented. In an attempt to find the sources of these interferences, several experiments were conducted. The first experiment involved the interferences produced with only the absorbing reagent. A series of calibration gases were passed through the absorbing reagent. These gases were 495 ppm carbon monoxide, 2.0 percent carbon dioxide, nitrogen dioxide, and a 5 ppmC hydrocarbon blend. These were compared to background air and a blank with no gas bubbled through it. Each gas was bubbled at 4.0 ℓ/min for twenty minutes and developed for methylene blue. No interference from these gases was observed.

A second experiment investigated the interferences from individual exhaust gas components on sulfide ion doped absorbing reagent. The gases used were carbon monoxide, carbon dioxide, compressed air, a hydrocarbon blend, sulfur dioxide and NO_x. Each of these gases were passed through a separate impinger filled with the doped absorbing reagent for twenty minutes at 4.0 ℓ/min. These were then compared to the doped absorbing reagent after development for methylene blue. Table 26 shows the results of this experiment. NO_x at 3000 ppm and sulfur dioxide at 5 ppm were found to quench the production of methylene blue.

TABLE 26. THE EFFECT OF INDIVIDUAL EXHAUST COMPONENTS ON THE DEVELOPMENT OF METHYLENE BLUE

Gas	Sample	Gas Conc., ppm	Absorbance	Methylene Blue Apparent Sulfide Ion Conc., µg/mℓ
Doped absorbing reagent	1		0.716	0.646
	2		0.708	0.638
Carbon dioxide	1	29,900	0.711	0.641
Carbon monoxide	1	2,709	0.704	0.634
Doped absorbing reagent	1		0.552	0.492
	2		0.560	0.500
Air	1		0.574	0.513
Hydrocarbon	1	168	0.554	0.494
Sulfur dioxide	1	5	0.461	0.408
NO_x	1	3,460	0.247	0.213
Doped absorbing reagent	1		0.648	0.582
	2		0.654	0.587
NO_x	1	315	0.666	0.599
	2	315	0.621	0.557
Sulfur dioxide	1	5	0.484	0.429
	2	5	0.533	0.475

A third experiment was designed to check the interference of anions in the development of methylene blue. Sodium salts of sulfate, thiosulfate, and bisulfite ions were used. Each of these anions was added to separate solutions of sulfide ion doped and undoped absorbing reagent. The solutions were then developed for methylene blue and compared to the doped absorbing reagent. Thiosulfate and bisulfite was investigated to determine the specific source of the sulfur dioxide interference. The results are shown in Table 27. Only bisulfite ion and thiosulfate ion caused a negative interference.

Finally, an additional experiment was conducted to help determine the source of sulfur dioxide interference. Approximately 2.5 ft^3 of 5 ppm sulfur dioxide was passed through an impinger filled with the zinc acetate absorbing reagent. This operation was then repeated six times. A 1 mℓ aliquot of the standard sulfide ion solution was added to two of these impingers. To two others, 5 mℓ were added. All six were developed for methylene blue. These were then compared to similar concentrations of sulfide ion solution doped absorbing reagent that did not undergo sulfur dioxide bubbling. These values are shown in Table 28. Again, the absorbance for methylene blue was decreased by the presence of sulfur dioxide.

TABLE 27. THE EFFECT OF ANIONS ON THE DEVELOPMENT OF METHYLENE BLUE

Anion	Sample	Absorbance	Apparent Sulfide Ion Conc., μg/mℓ
		doped with hydrogen sulfide	
Sulfate ion	1	0.238	0.205
	2	0.241	0.207
Thiosulfate ion	1	0.207	0.177
	2	0.211	0.181
Bisulfite ion	1	0.239	0.206
	2	0.231	0.198
Doped absorbing reagent		0.241	0.207
		undoped	
Sulfate ion	1	0.001	
	2	0.000	
Thiosulfate ion	1	0.009	
	2	0.004	
Bisulfite ion	1	0.007	
	2	0.005	

TABLE 28. THE EFFECT OF SULFUR DIOXIDE INTERFERENCE ON THE DEVELOPMENT OF METHYLENE BLUE

Sulfide ion added, mℓ	Absorbance	Apparent Sulfide ion conc., μg/mℓ
	Sulfur dioxide passed through absorbing reagent	
1	0.067	0.055
1	0.070	0.057
5	0.463	0.410
5	0.326	0.284
0	0.002	0.000
0	0.006	0.000
	No sulfur dioxide passed through absorbing reagent	
1	0.082	0.067
5	0.583	0.521

QUALIFICATION EXPERIMENTS

A 1972 Plymouth Fury with a 360 V8 engine was used in the qualification experiments for hydrogen sulfide. No catalyst was present on this vehicle. The baseline emission rate for this vehicle was below the detection limits for the analytical procedure. This baseline was established with three separate hot FTP driving cycles. Hydrogen sulfide was injected into the CVS with and without the vehicle. The concentration of hydrogen sulfide injected was 515 ppm. With the vehicle present, the hydrogen sulfide was injected into the raw exhaust stream just before entering the CVS. Samples were taken from the dilute stream and passed through a buffered zinc acetate absorbing reagent. The samples were then analyzed with a Beckman spectrophotometer. The data for this experiment is given in Tables 29 and 30. Essentially 100 percent recovery was obtained without exhuast. However, a decrease of almost 10 percent was observed with exhaust. These results include corrections for baseline exhaust and background air concentrations of hydrogen sulfide.

RESULTS AND CONCLUSIONS

The measurement of hydrogen sulfide in dilute exhaust can be conducted with a colorimetric technique. Hydrogen sulfide is trapped in a buffered zinc acetate solution. Upon treatment with N, N dimethyl p-phenylene

TABLE 29. HYDROGEN SULFIDE GASEOUS RECOVERY BY DIRECT CVS INJECTION

Nominal Flow Rate, ft^3/min						
H_2S blend	CVS	Run	Sample	Calculated ppm H_2S Dilute	Observed ppm *	Percent Recovery H_2S
0.35	320	1	1	0.62	0.64	102.7
0.35	320	1	2	0.62	0.67	107.5
0.35	320		3	0.62	0.66	105.9
0.35	320	2	1	0.65	0.73	111.9
0.35	320	2	2	0.65	0.74	113.4
0.35	320	2	3	0.65	0.72	110.4
0.35	320	3	1	0.69	0.74	107.1
0.35	320	3	2	0.69	0.74	107.1
0.35	320	3	3	0.69	0.73	105.6
					Average	108.0

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*This value is corrected for the background.

TABLE 30. HYDROGEN SULFIDE GASEOUS RECOVERY FROM DILUTE EXHAUST BY DIRECT CVS INJECTION

		Hydrogen Sulfide Concentration, ppm			
Run	Sample	Calculated Amount Injected	Observed (exhaust+air)*	(air only)	Percent Recovery
1	1	0.66	0.58	0.01	87.0
1	2	0.66	0.60	0.01	90.1
1	3	0.66	0.60	0.01	90.1
2	1	0.68	0.61	0.01	87.7
2	2	0.68	0.64	0.01	92.0
2	3	0.68	0.64	0.01	92.0
3	1	0.65	0.59	0.00	90.5
3	2	0.65	0.54	0.00	82.8
3	3	0.65	0.61	0.00	93.6
				Average	89.5

---

*This value is corrected for the baseline concentration in exhaust.

diamine sulfate, and ferric ammonium sulfate, cyclization occurs to form methylene blue. The analysis is conducted spectrophotometrically at 667 nm. The minimum detectable concentration is 0.01 ppm.

Several experiments were conducted to determine the interferences and their sources in the analysis of hydrogen sulfide. Such individual exhaust gas components as carbon dioxide, carbon monoxide, and hydrocarbons show no effect on the absorbance of methylene blue. NO_x showed a negative interference only at concentrations ten times higher than that expected in dilute exhaust. Sulfur dioxide also shows a negative interference at 5 ppm. To determine the source of the sulfur dioxide interference, several experiments were conducted. These experiments were discussed in a previous section. In all cases with sulfur dioxide present, the absorbance for methylene blue was decreased. Also, a broad peak was observed from 525 nm to 675 nm in the visible region of the spectrum. The presence of bisulfite ion and thiosulfate ion produces the same effect. Bisfulfite ion can be produced from sulfur dioxide by the simplified reaction:

$$SO_2 + H_2O \longrightarrow HSO_3^- + H^+$$

Thiosulfate ion forms bisulfite ion in strongly acidic solutions:

$$S_2O_3^= + H^+ \longrightarrow HSO_3^- + S$$

Sulfate ion shows no interference.

The presence of sulfur dioxide in the absorbing reagent apparently quenches the production of methylene blue from hydrogen sulfide. Sulfur dioxide acts as an oxidizing agent toward hydrogen sulfide(free sulfur is formed) and as a reducing agent toward methylene blue, an oxidation-reduction indicator. Sulfur dioxide dissolves in water to form sulfurous acid. Since the presence of bisulfite ion produces a similar interference, the decrease in the absorbance for methylene blue is probably due to this reaction. The elimination of the sulfur dioxide interference is not an easy task. It should be recognized, however, that an apparent decrease in concentration of hydrogen sulfide is observed when sulfur dioxide is present.

The sampling parameters used for the collection of hydrogen sulfide in dilute exhaust were determined partly by necessity and partly by consistency. The sample flow rate of 4.0 ℓ/min was selected to insure a sufficient sample for analysis although the lower flow rate showed a slightly better collection efficiency in the first bubbler. The use of an ice bath to cool the absorbing reagent was selected for simplicity and consistency with the other analytical procedures which require an ice bath. The absorbing reagent temperature produces little or no effect on the collection efficiency for ambient temperature sampling, but sample breakthrough is possible at exhaust gas sampling temperatures greater than ambient conditions. Two impingers filled with buffered zinc acetate absorbing reagent are necessary for complete sample recovery. These parameters are sufficient to collect sample concentrations within the detection limits of the procedure from dilute exhaust.

The qualification experiments revealed an average CVS recovery in dilute exhaust of 89.5 percent. No losses were observed without the vehicle (no exhaust); therefore, a 10 percent loss of hydrogen sulfide can be expected in the presence of dilute exhaust. Since hydrogen sulfide reacts with sulfur dioxide under the proper conditions, the most important source of hydrogen sulfide lost in the CVS is probably from the sulfur dioxide present in dilute exhaust.

The effect of light on the stability of methylene blue was determined for four samples over a period of weeks. Both concentrations were stable for about two days whether exposed to the light or kept in the dark. The high concentration samples required a slightly longer time to develop (30 minutes) than the low concentration samples. Both concentrations exhibited a steady decay with time after the initial development. The sample decay was independent of the exposure to light. At 10 days for the low concentrations and 20 days for the high concentrations, an increase in the apparent concentration was observed. Inspection of the entire wavelength extinction curve showed that the absorbance was no longer due to methylene blue but some other constituent in the solution. No attempts were made to specifically define the source of this absorbance. However, the solutions were found to be stable in the light for at least several hours after development in the dark. If samples cannot be processed by this time, it is recommended that they be discarded because of the difficulty in preserving the sample integrity.

Two possible absorbing reagents were compared to determine the best one for the analysis. Zinc acetate was selected rather than cadmium hydroxide. Ease of use, reduced toxicity, and photochemical stability were the criteria for this selection.

This procedure provides a sensitive method for the analysis of hydrogen sulfide in dilute exhaust. A single sample requires five to ten minutes to add the reagents, thirty minutes to develop, and three to five minutes to analyze the sample. Absorbing reagent stability helps to simplify the analysis and makes this procedure ideal for analyzing a large number of samples.

SECTION 8

TOTAL CYANIDE PROCEDURE

LITERATURE SEARCH

Hydrogen cyanide is a flammable, toxic, colorless liquid at room temperature, with the characteristic odor of bitter almonds. Some synonyms for hydrogen cyanide are hydrocyanic acid, prussic acid, and formonitrile. Hydrogen cyanide is a covalent molecule and is capable of dissociation in an aqueous solution, as are the hydrogen halides. Hydrogen cyanide (HCN) has a molecular weight of 27.03, a boiling point of 25.70°C, and a melting point of -13.24°C. It is a linear molecule with C-H and C≡N bond distances of 1.06 and 1.15 Å, respectively. It is a weak monoprotic acid with a dissociation constate of 2.1×10^{-9}. This highly poisonous compound is a respiratory inhibitor and irreversible combines with the iron complex in the blood, stopping the oxidation processes in tissue cells and causing death by asphyxiation. Commercially, hydrogen cyanide is prepared by reacting methane, ammonia, and air over a platinum catalyst at 1000-1200°C, by the reaction of nitric oxide and gasoline at 1400°C, the reaction of hydrocarbons, ammonia, and oxygen at 600-1500°C, and many other methods. Reactions similar to these may be responsible for the hydrogen cyanide produced in exhaust.

Cyanogen is a flammable, toxic, colorless gas at room temperature and like hydrogen cyanide has the characteristic odor of bitter almonds. Some synonyms for cyanogen are dicyan, oxalic acid, dinitrile, and oxalonitrile. Pure cyanogen is stable, although the impure gas may polymerize to paracyanogen at 300° to 500°C or by exposure to ultraviolet light. Cyanogen dissociates into CN radicals and can oxidatively add to lower valent metal atoms, giving dicyano complexes. It resembles halogens in the disproportionation reaction in basic solution:

$$(CN)_2 + 2OH^- \longrightarrow CN^- + H_2O$$

Cyanogen (C_2N_2) has a molecular weight of 52.04, a freezing point of -27.9°C, and a boiling point of -21.17°C. It is symmetrical and linear molecule with a C-C bond distance of 1.37 Å and a C≡N bond distance of 1.13 Å. Its physiological effect on living tissue is similar to that of hydrogen cyanide. Cyanogen is prepared by many methods: air oxidation of hydrogen cyanide over a silver catalyst at 300-600°C, passage of hydrogen cyanide over cuprous oxide at ambient temperatures, reaction of hydrogen cyanide and chlorine over a surface-active material such as activated charcoal at >700°C, and many others. In all cases above, cyanogen is produced from hydrogen cyanide. Although none of these are exactly applicable for an automotive system, a similar process may be responsible for any cyanogen that is produced.

The analyses for hydrogen cyanide, cyanogen, and/or cyanide ion has been performed by several basic analytical techniques: titration, colorimetry, specific ion electrode, and gas chromatography. The Liebig determination of cyanide ion by titration with silver ion was discarded as a means of analysis because of the low concentrations that were expected from exhaust samples. Colorimetry has previously been used by SwRI and has been found to be manpower intensive. An alternative procedure was sought with this factor in mind. The best means of analysis was with either a specific ion electrode or a gas chromatograph.

Three acceptable procedures were selected from the literature. Sekerka and Lechner(81) reported the use of a cyanide ion-selective electrode for the analysis of cyanide ion in waste water. The specific ion electrode was used in conjunction with a colorimetric technique to determine the reliability of the procedure. The samples were collected in sodium or potassium hydroxide and analyzed potentiometrically. The minimum detectable limit reported was about 2 ppb. The second technique required the use of Tedlar bag samples and subsequent analysis with a gas chromatograph using a nitrogen phosphorus detector (NPD). The third technique reported by Valentour et al (82) was used with biological samples (blood, urine, and gastric contents). The samples were collected in sodium or potassium hydroxide and the trapped cyanide ion was reacted with chloramine-T to produce cyanogen chloride. The cyanogen chloride was then analyzed with a gas chromatograph using an electron capture detector (ECD). After preliminary experiments, the final analytical procedure selected was a significant modification of the Valentour et al procedure.

PROCEDURAL DEVELOPMENT

Attempts to analyze hydrogen cyanide and cyanogen separately were unsuccessful and the details are reported below. The inability to analyze hydrogen cyanide and cyanogen separately led to consideration of several specific procedures for the analysis of hydrogen cyanide and cyanogen in the form of cyanide ion.

Initially, it was decided to determine the concentration of hydrogen cyanide and cyanogen by collecting a bag sample of the dilute exhaust and analyzing it with a gas chromatograph using a nitrogen phosphorous detector. This detector was selected because of its specificity to carbon-nitrogen compounds. Hydrogen cyanide and cyanogen can be resolved with a 6' X 1/4" O.D. glass column packed with 100/120 mesh Porapak QS. Isothermal column temperature operation at 50°C and a helium carrier gas flow rate of 60 ml/min were the column conditions. A glass lined injector and interface was also used to preserve sample integrity.

Bag stability experiments with hydrogen cyanide and cyanogen were conducted to determine if sample integrity could be maintained over a short period of time. Bag stability is necessary due to time required to collect the sample and the subsequent waiting period before the sample can be analyzed. The bag sample lifetime should be at least two hours after a sample is collected. Clear and aluminum foil tape covered Tedlar plastic bags were used to conduct bag stability experiments. Dark bags (aluminum foil tape covered) were tested to determine the effect of photochemical decomposition on hydrogen cyanide and cyanogen.

A list of bag stability experiments which were conducted is shown in Table 31. Each bag contained approximately one cubic foot of the diluent gas. Experiments were conducted with nitrogen, air, dilute exhaust and humid nitrogen. Dilute exhaust was selected at random from bag samples generated during other tests, and humid nitrogen was generated by passing nitrogen through an impinger containing deionized water. Hydrogen cyanide and/or cyanogen were then added to each bag to give a nominal concentration of about 2 ppm. At twenty to thirty minute intervals, 5 mℓ of the gas was removed with a glass gas-tight syringe and injected into the gas chromatograph. The percent change in the concentration was then calculated using the initial injection. Figures 26 through 30 show the effect of elapsed time on the stability of hydrogen cyanide and cyanogen. Figure 26 demonstrates the stability of hydrogen cyanide in clear and dark bags with a variety of atmospheres. Peak areas for hydrogen cyanide remained within the nominal range of injection variability for at least 80 minutes, and no definite trends were observed. (The nominal range of injection variability was set at ± 7 percent and is indicated in all Figures by a dotted line.) On the other hand, cyanogen showed a considerable percent loss in the clear bags with both nitrogen and exhaust (Figure 27). In the dark bag, cyanogen remained stable except in the presence of exhaust.

Figures 28 and 29 show the effect of a blend of hydrogen cyanide and cyanogen in clear and dark bags with the various atmospheres. Again, hydrogen cyanide was stable within the limits of injection variability for a short period of time. In both cases, hydrogen cyanide was stable on the order of about 60 minutes. Cyanogen behaved similarily to hydrogen cyanide in the clear bag, but a steady decrease in concentration was observed in all atmospheres with the dark bag.

In humid nitrogen (Figure 30) there was a 70 percent loss of hydrogen cyanide after only 20 minutes. After this initial loss, the level of hydrogen cyanide remained relatively constant. Cyanogen under the same conditions showed only a slight decrease in concentrations.

The short bag lifetime of hydrogen cyanide and cyanogen prevent the use of grab samples of exhaust. At this point, the alternative procedures were investigated for the analysis of hydrogen cyanide and cyanogen. These techniques required samples to be collected in an aqueous solution.

At the same time the work with bag samples was underway, efforts to develop a procedure using the specific ion electrode were being conducted. Potassium cyanide standard solutions were prepared with 0.1M potassium hydroxide. A calibration curve was to be determined by plotting the measured potential in millivolts as a function of the log of the cyanide ion concentration. Instability of the potentiometric measurement was observed in all concentration ranges, especially in the low concentration range. Attempts to improve the electrode stability and potential drift were

TABLE 31. EXPERIMENTS CONDUCTED FOR HCN AND C_2N_2 BAG STABILITY

Compound	Clear Bags			Dark Bag		
	Nitrogen	Air	Exhaust	Nitrogen	Air	Exhaust
HCN	X	X	X	X	X	X
C_2N_2	X	X	X	X	X	X
HCN & C_2N_2		X	X	X	X	X
HCN & C_2N_2*				X		

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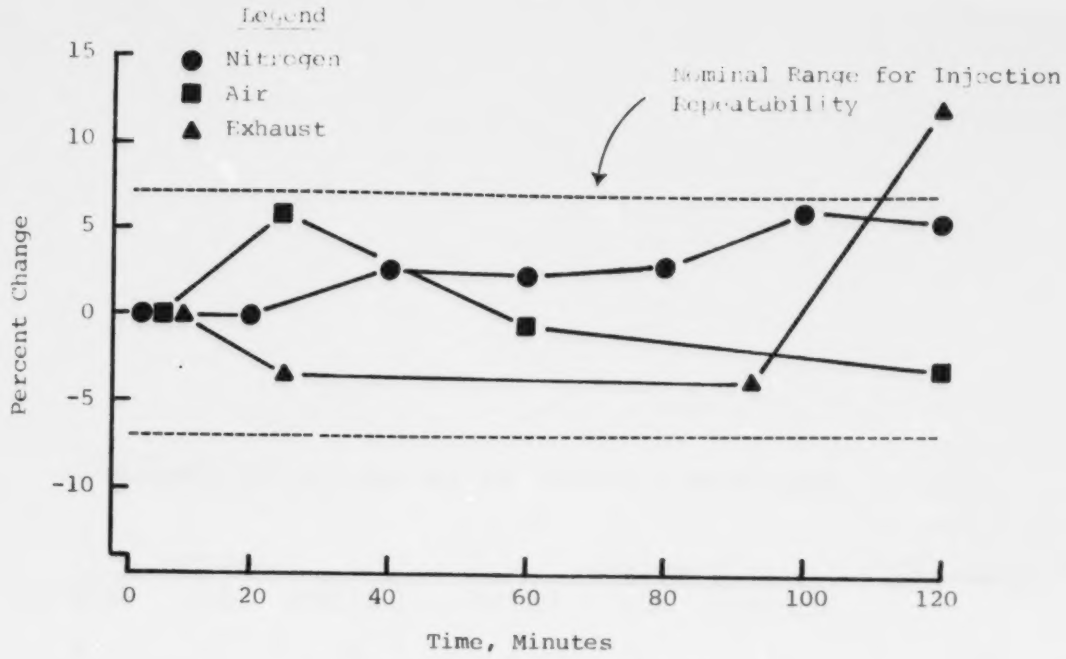
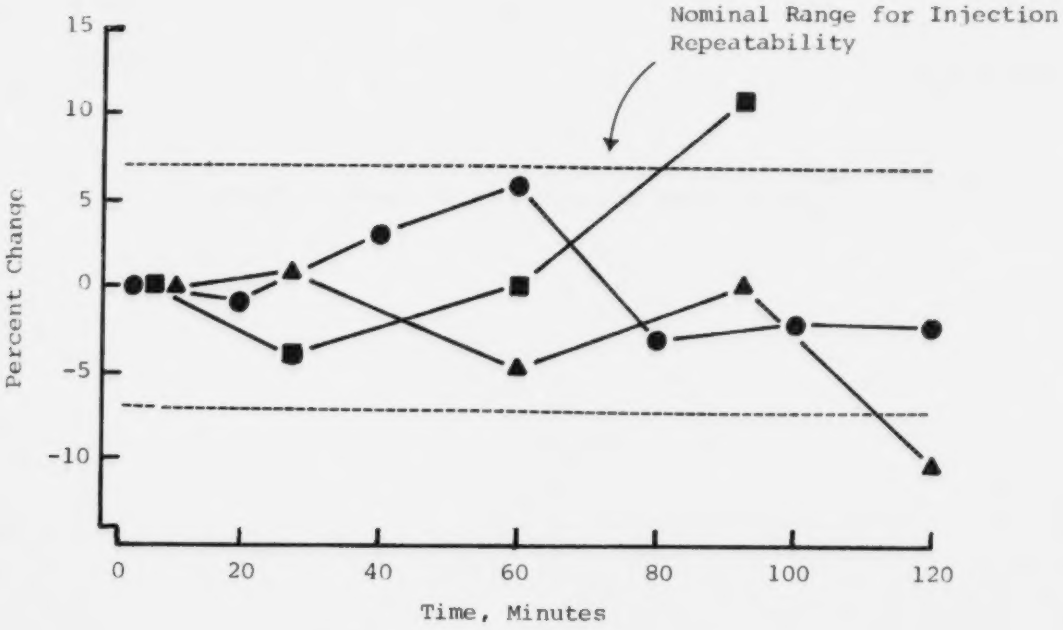
* Blend of hydrogen cyanide and cyanogen in humid nitrogen

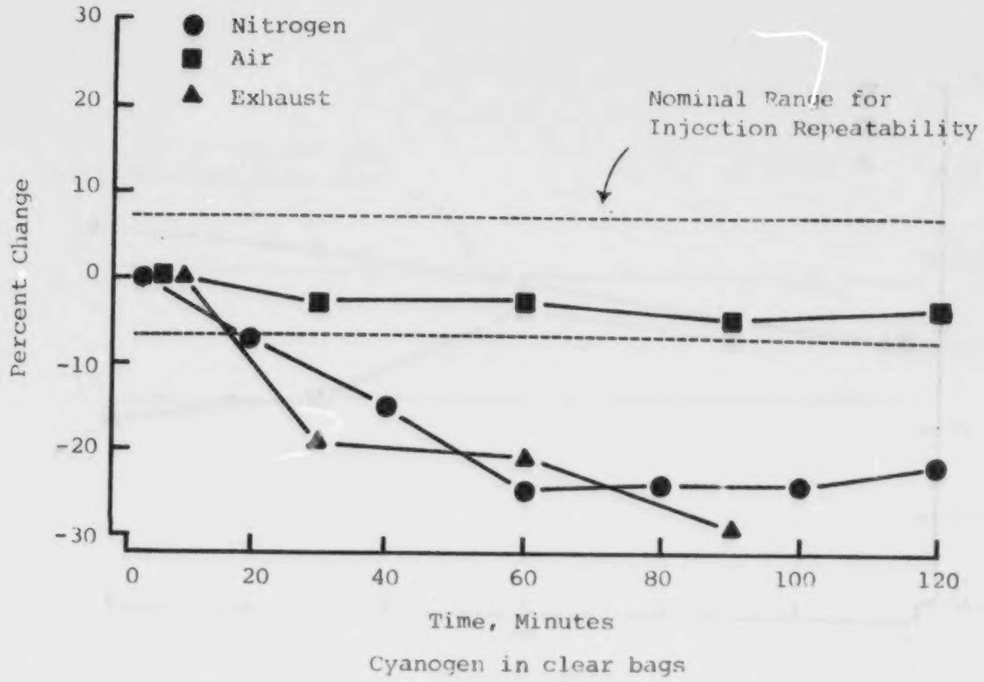


Hydrogen cyanide in clear bags

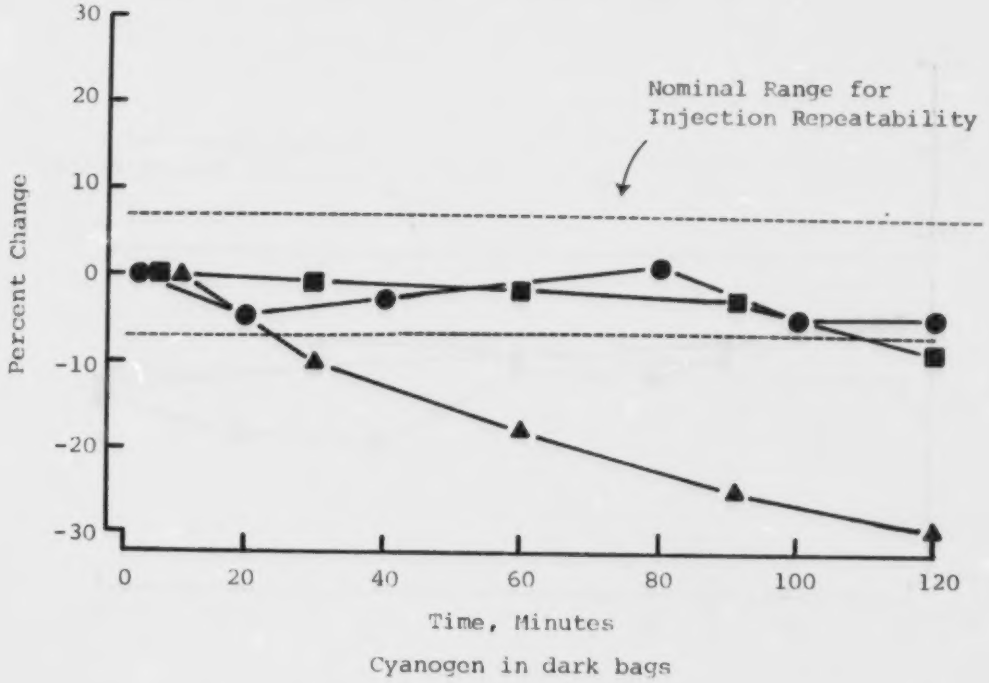


Hydrogen cyanide in dark bags

Figure 26. Effect of elapsed time on hydrogen cyanide in clear and dark bags.

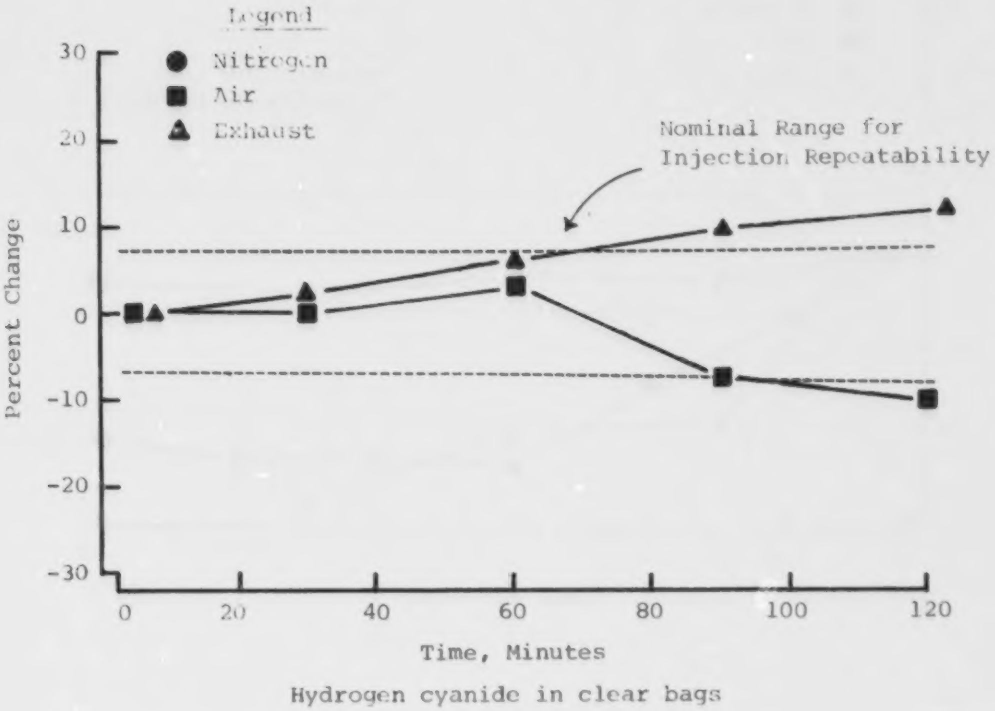


Cyanogen in clear bags

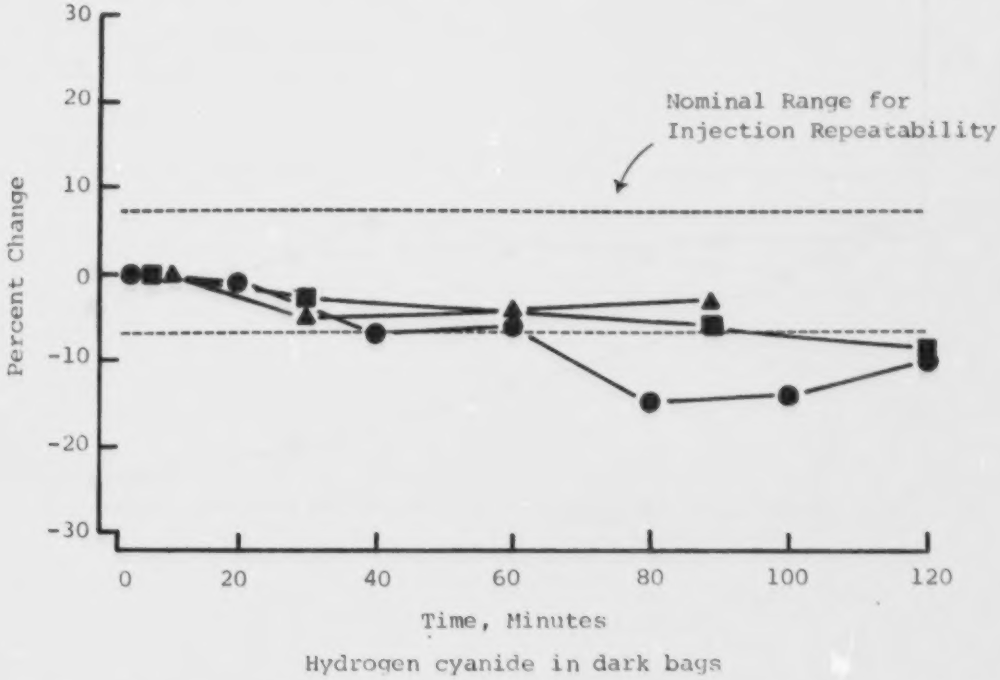


Cyanogen in dark bags

Figure 27. **The effect of elapsed time on cyanogen in clear and dark bags.**

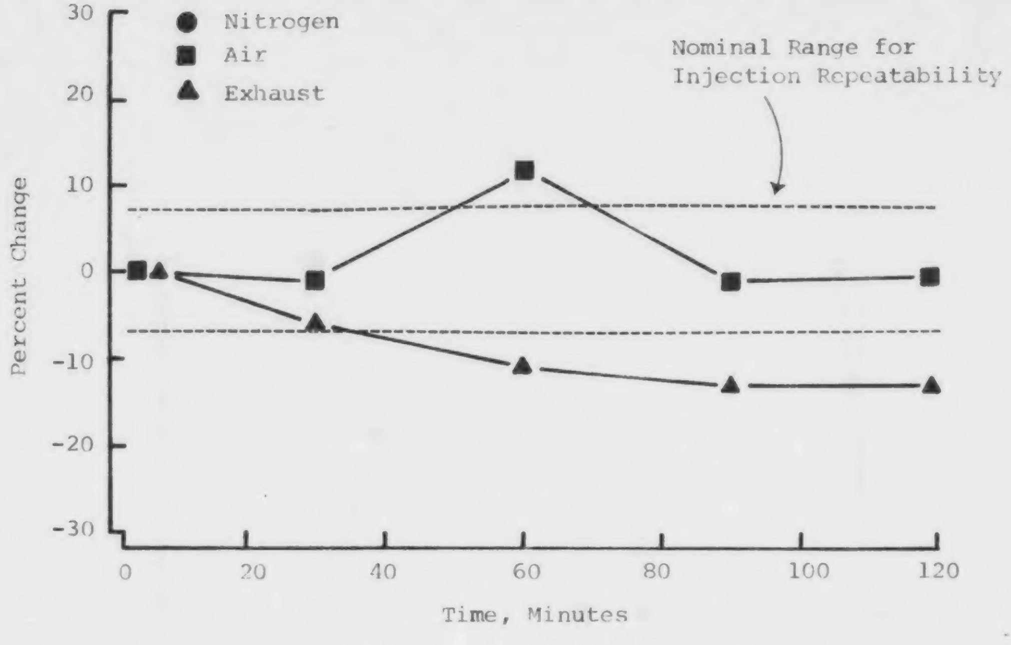


Hydrogen cyanide in clear bags

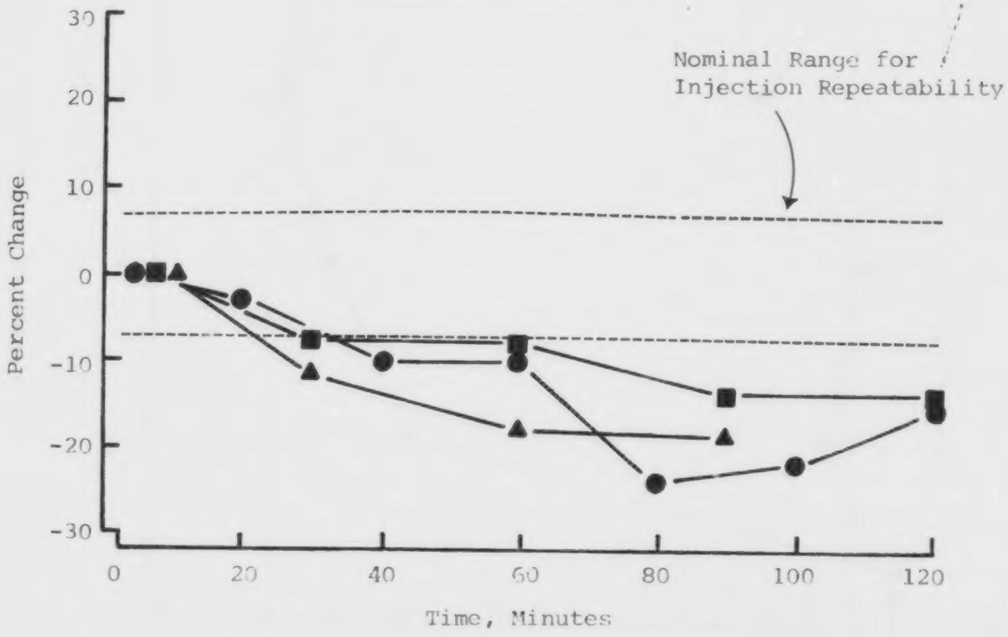


Hydrogen cyanide in dark bags

Figure 28. The effect of elapsed time on hydrogen cyanide in a blend of hydrogen cyanide and cyanogen in clear and dark bags.



Cyanogen in clear bags



Cyanogen in dark bags

Figure 29. The effect of elapsed time on cyanogen in a blend of hydrogen cyanide and cyanogen in clear and dark bags.

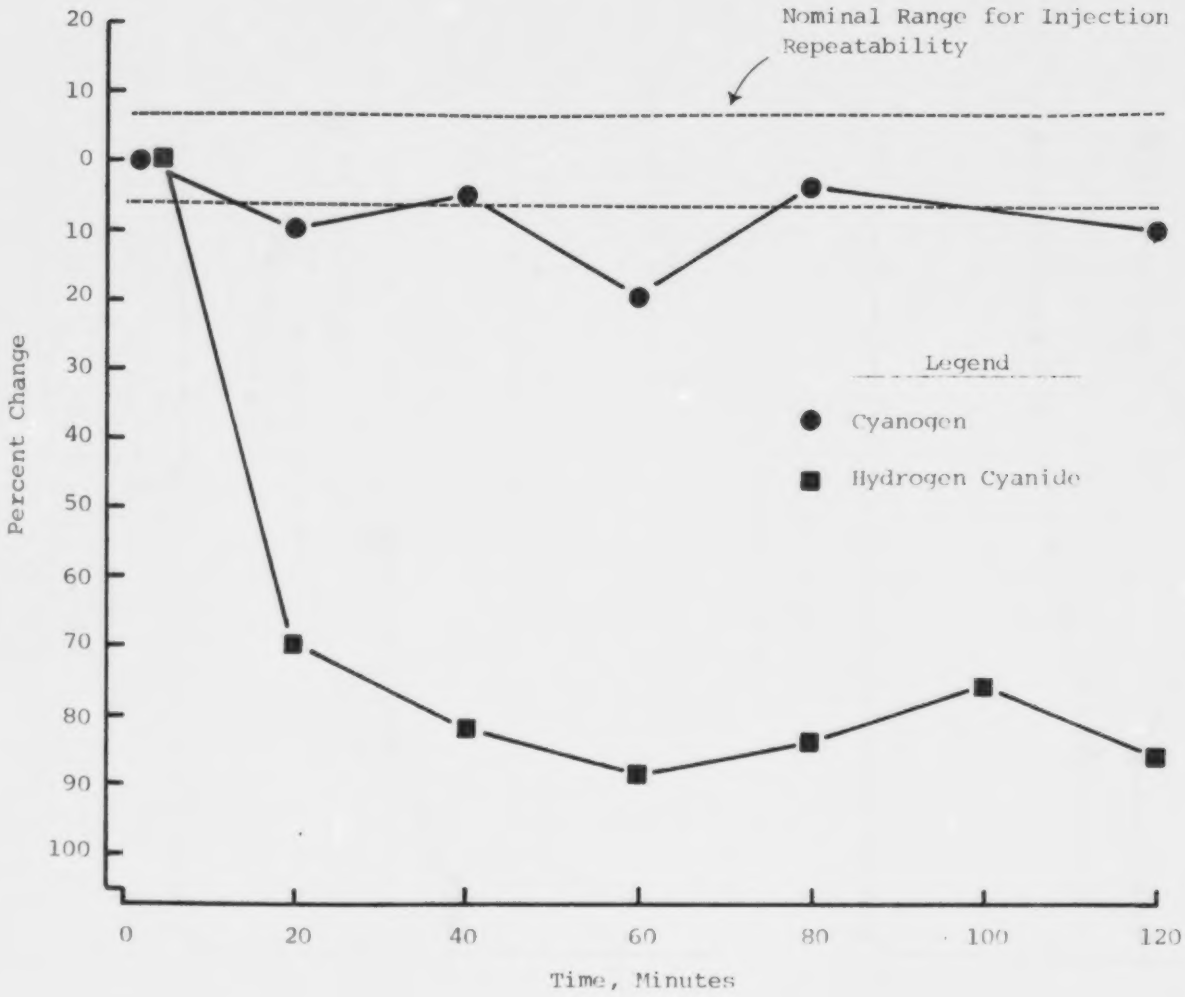


Figure 30. The effect of elapsed time on hydrogen cyanide and cyanogen in a dark bag with humid nitrogen.

unsuccessful. Efforts using the specific ion electrode were abondoned for another procedure using gas chromatography. A gas chromatograph procedure which did not require bag samples for the collection of hydrogen cyanide and cyanogen was investigated. This procedure used a chemical collection of cyanide ion in sodium or potassium hydroxide. Initially, the analysis was to be conducted by reacting chloramine-T with the trapped cyanide ion in an acid buffered solution to produce cyanogen chloride. Cyanogen chloride was then extracted by hexane and analyzed with an electron capture detector. The electron capture detector was chosen because of its high sensitivity and selectivity to halogenated compounds and relative insensitivity to hydrocarbons. Problems with impurities in the hexane caused broad peaks with an excessive analysis time. To eliminate the problem, the following items were tried:

1. Temperature program sequences
2. Column backflush
3. Column changes
    A. 6' X 1/4" OD glass column packed with 100/120 mesh Porapak QS
    B. 6' X 1/4" OD stainless steel column packed with 50/80 mesh Porapak Q
    C. 6' X 1/4" OD stainless steel packed with 7 percent Hallcomid M-18 on 90/100 mesh Anakrom ABS
4. Hexane purification with charcoal
5. Other extracting solvents (i.e., cyclohexane, etc.)

None of these proved to be satisfactory and long analysis times were the result.

A modification of the above procedure was tried by eliminating the hexane layer and conducting the analysis in the same manner as described above, except that the sample was placed in an air tight reaction vial with a 1 mℓ head space and a septum cap. A sample development period of 5 minutes was required. After vigorously shaking the vial for 5 seconds, 100 μℓ of the head space was injected into the gas chromatograph. An electron capture detector was used for the analysis. As a result of this modification, a rapid analysis time was achieved. The finalized analytical procedure is included as an attachment to this report.

VALIDATION EXPERIMENTS

After selecting an analytical method, validation experiments were conducted to determine detector linearity, detection limits, injection repeatability, stability of reagents and sample, sampling parameters, etc. Once the validations experiments were complete, the procedure was considered ready for testing.

Collection parameters were determined with a series of experiments designed to check sample flow rates, absorbing reagent concentration, absorbing reagent temperature, impingers or fritted glass bubblers, and collection efficiency. All of these experiments were conducted with hydrogen cyanide.

The first experiments conducted were to determine the effects of stopper tip, sample flow rate, and reagent concentration on the collection efficiency. The results of these experiments are shown in Table 32. A set of three of the same type collection devices (impinger or fritted glass tipped bubblers) were filled with 1.0N or 0.1N potassium hydroxide. A hydrogen cyanide calibration blend that contained a nominal 2 ppm concentration in a balance of nitrogen was passed through the absorbing reagent at 1.0 and 4.0 ℓ/min. Each experiment was repeated three times. All of these experiments were conducted in a special blending building, which was external to the main building. This building did not have the normal temperature controls within the building and the ambient temperature fluctuated with the weather. The room temperature ranged from about 15 to 30°C during the experiments.

After careful examination of the data, several trends can be observed. First, in all cases, more cyanide ion was collected with the stronger absorbing reagent. Secondly, more cyanide ion was trapped with the impinger than the fritted glass tipped bubbler. The possible reason for this was a flow restriction due to the fritted glass tip. Finally, the higher flow rate produced more consistent results with both concentrations of the absorbing reagent.

The next set of experiments took into account the results of the first set plus the effect of reagent temperature. Five sets of three impingers filled with 25 mℓ each of 1.0N potassium hydroxide absorbing reagent were used. The sample flow rate was set at 4.0 ℓ/min. The first set of impingers was sampled at ambient room temperature (16-29°C) and a second set of impingers was sampled at ice bath temperatures. The sample collection efficiency for the ambient temperature experiments showed a high degree of variability. The collection efficiency for the first impinger was between 70 and 100 percent. At this temperature three impingers would be necessary to collect the entire sample even at low concentrations. With the ice bath, the first bubbler was sufficient to collect the entire sample as well as giving more consistent results. The data for these experiments is shown in Table 33.

Detector linearity was demonstrated for two cyanide ion concentration ranges. A linear response was observed in the 0 to 2 and the 0 to 10 µg CN^-/mℓ ranges. Table 34 and Figures 31 and 32 show the detector linearity. All samples are expected to be within this concentration range. If samples are obtained that are not in these regions, the samples will be diluted to a concentration which falls within the linear response of the detector.

Sample injection reproducibility is essential for any gas chromatography technique which does not involve the use of internal standard. To establish sample injection reproducibility, two nominal cyanide ion concentrations, 2.0 and 0.2 µg/mℓ, were used. Five separate samples of each concentration were developed and injected. The results are shown in Table 35.

Three separate experiments involving the sample storage and sample

TABLE 32. THE EFFECT OF STOPPER TIP AND ABSORBING REAGENT CONCENTRATION ON COLLECTION EFFICIENCY AT ROOM TEMPERATURE

			μg CN^-/ft^3 sample					
			1.0 N KOH			0.1 N KOH		
Collection Device	Sample Flow	Run	1	2	3	1	2	3
impinger	1.0	1	93.47	7.71	1.55	50.02	7.08	6.21
impinger	1.0	2	65.71	9.26	2.61	60.13	6.06	0.00
impinger	1.0	3	74.28	6.38	0.00	49.92	6.16	5.48
		Avg	77.82	7.78	1.39	53.36	6.43	3.90
bubbler	1.0	1	11.44	0.00	0.00	4.64	1.40	2.73
bubbler	1.0	2	0.00	0.00	0.00	1.11	0.00	0.00
bubbler	1.0	3	0.00	0.00	0.00	2.57	0.00	0.00
		Avg	3.81	0.00	0.00	2.77	0.47	1.37
impinger	4.0	1	37.15	5.35	0.67	29.60	3.53	0.77
impinger	4.0	2	29.18	3.18	0.60	27.20	3.24	1.08
impinger	4.0	3	28.96	2.90	0.35	27.24	2.69	0.62
		Avg	31.76	3.81	0.54	28.01	3.15	0.82
bubbler	4.0	1	20.20	1.41	0.00	15.14	1.85	0.00
bubbler	4.0	2	25.30	2.96	3.52	7.42	0.85	0.00
bubbler	4.0	3	18.94	2.10	0.32	16.21	1.78	0.00
		Avg	21.48	2.16	1.28	12.92	1.49	0.00

TABLE 33. THE EFFECT OF ABSORBING REAGENT TEMPERATURE ON HCN COLLECTION EFFICIENCY

Date	Run	Absorbing Reagent Temperature °F	Absorbing Reagent Temperature °C	Time min	Flow ℓ/min	μg CN⁻/ft³ 1	μg CN⁻/ft³ 2	μg CN⁻/ft³ 3	μg CN⁻/ft³ Total	μg CN⁻/m³ 1	μg CN⁻/m³ 2	μg CN⁻/m³ 3	μg CN⁻/m³ Total	ppm CN⁻ 1	ppm CN⁻ 2	ppm CN⁻ 3	ppm CN⁻ Total
10/11/77	1	72	22	20	4.0	48.61	4.39	0.00	53.00	1716.6	155.0	0.0	1871.7	1.54	0.14	0.00	1.68
10/13/77	2	61	16	20	4.0	64.98	0.00	0.00	64.98	2294.7	0.0	0.0	2294.7	2.07	0.00	0.00	2.07
10/17/77	3	63	17	20	4.0	35.27	7.02	3.76	46.05	1245.5	247.9	132.8	1626.2	1.12	0.22	0.12	1.46
10/17/77	4	73	23	20	4.0	30.06	10.33	3.95	44.34	1061.6	364.8	139.5	1565.8	0.97	0.33	0.13	1.43
10/17/77	5	84	29	20	4.0	24.46	8.09	2.26	34.81	863.8	285.7	79.8	1229.3	0.80	0.26	0.07	1.13
					Avg	40.68	5.97	1.99	48.64	1436.7	210.7	70.3	1717.4	1.30	0.19	0.06	1.55
10/12/77	1	32	0	20	4.0	55.76	0.00	0.00	55.76	1968.1	0.0	0.0	2147.1	1.77	0.00	0.00	1.77
10/12/77	2	32	0	20	4.0	51.96	0.00	0.00	51.96	1834.9	0.0	0.0	1834.9	1.67	0.00	0.00	1.67
10/12/77	3	32	0	20	4.0	57.86	0.00	0.00	57.86	2043.3	0.0	0.0	2043.3	1.86	0.00	0.00	1.86
10/12/77	4	32	0	20	4.0	54.00	0.00	0.00	54.00	1907.0	0.0	0.0	1907.0	1.92	0.00	0.00	1.92
10/12/77	5	32	0	20	4.0	51.05	0.00	0.00	51.05	1802.8	0.0	0.0	1802.8	1.65	0.00	0.00	1.65
					Avg	54.13	0.00	0.00	54.13	1911.6	0.0	0.0	1947.2	1.77	0.00	0.00	1.77

TABLE 34. CALIBRATION CURVE LINEARITY AT SEVERAL CYANIDE CONCENTRATIONS

Test	Date	CN^- Conc. μg/mℓ	GC Attn	Sample height	Sample area	Background Corrected height	Background Corrected area
1	10/11/77	9.64	X256	45	4650	44	4600
		4.82	X256	26	2644	25	2594
		1.93	X256	11	1182	10	1132
		0.96	X256	5	583	4	533
		0.00	X256	1	50	0	0
2	10/12/77	9.64	X256	40	4102	40	4102
		4.82	X256	24	2448	24	2448
		1.93	X256	9	953	9	953
		0.96	X256	5	518	5	518
		0.00	X256	0	0	0	0
3	10/03/77	1.93	X64	80	7939	79	7816
		0.96	X64	42	4146	41	4023
		0.48	X64	19	1947	18	1824
		0.19	X64	8	817	7	694
		0.00	X64	1	123	0	0
4	10/04/77	1.93	X64	68	6813	68	6813
		0.96	X64	36	3538	36	3538
		0.48	X64	17	2027	17	2027
		0.19	X64	6	643	6	643
		0.00	X64	0	0	0	0

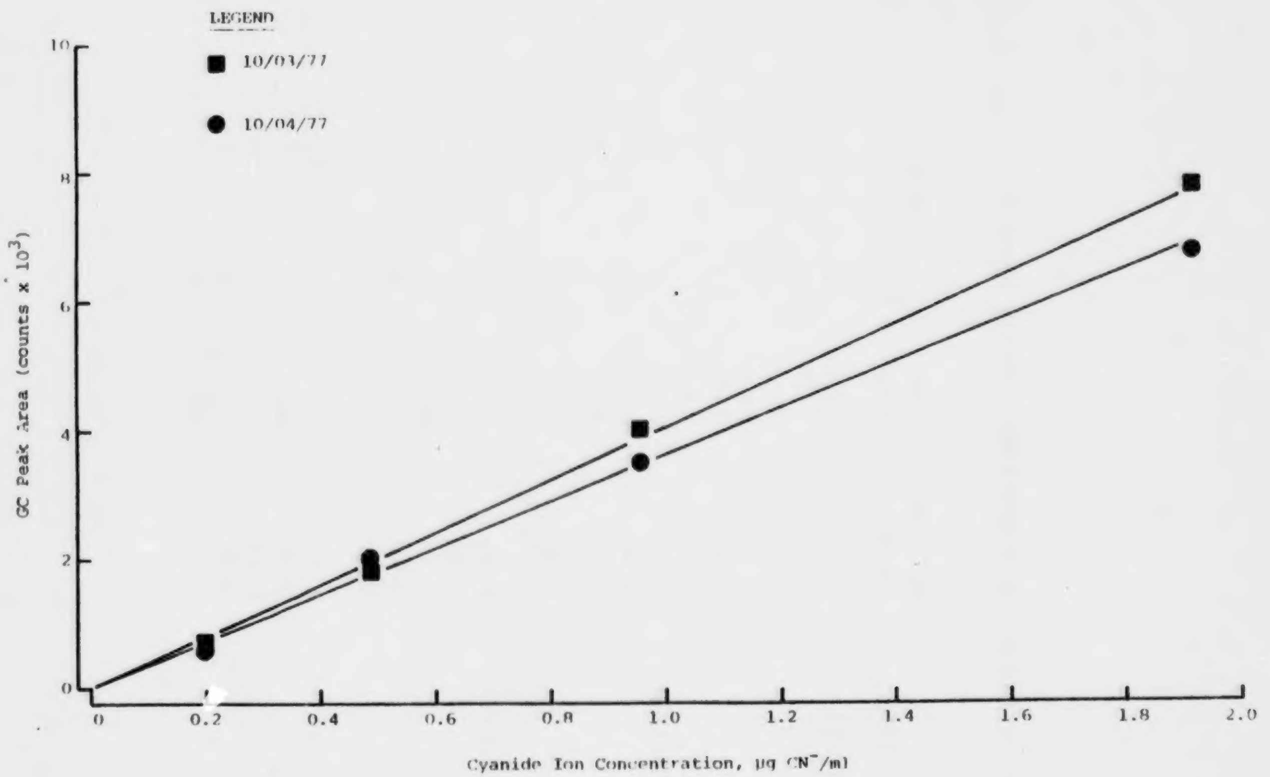


Figure 31. Total cyanide calibration curve at low concentrations (0-2 ppm).

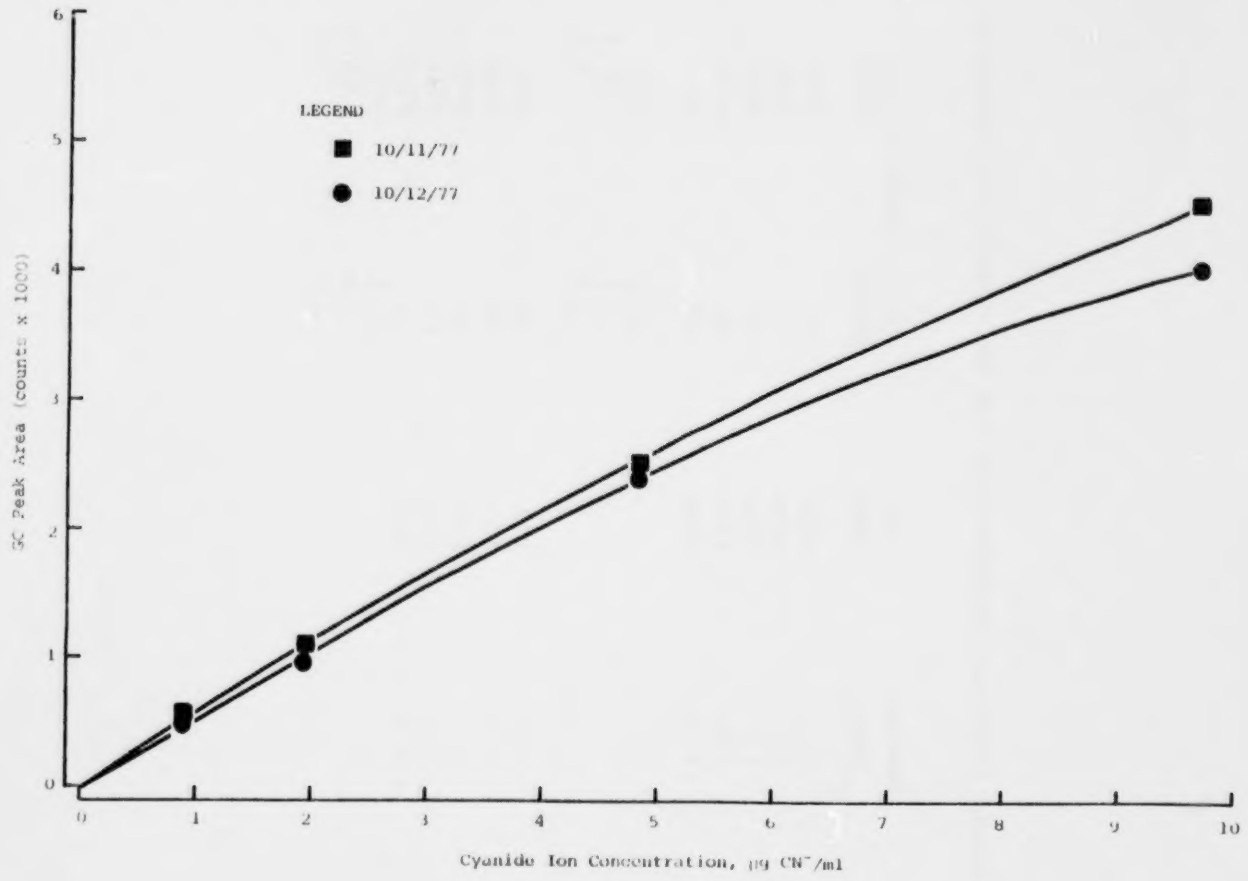


Figure 32. Total cyanide calibration curve at low concentrations (0-10 ppm).

TABLE 35. SAMPLE INJECTION REPEATABILITY FOR TWO CYANIDE CONCENTRATIONS

Sample	Nominal ppm	GC Attn	Peak Height	Peak Area
1	2.0	X256	62	6807
2	2.0	X256	60	6550
3	2.0	X256	61	6675
4	2.0	X256	61	6703
5	2.0	X256	63	6913
$\bar{x}$			61.4	6730
S_x			1.1	137.5
Cv			1.9	2.0
1	0.2	X32	66	6621
2	0.2	X32	70	7095
3	0.2	X32	68	6838
4	0.2	X32	65	6711
5	0.2	X32	64	6544
$\bar{x}$			66.6	6762
S_x			2.4	216.0
Cv			3.6	3.2

stability were also conducted. Three separate samples of known concentration were developed for the required time and injected as usual. At thirty minute intervals, 100 µl of the remaining head space was also injected. The decay of the peak areas for a two hour period is shown in Figure 33. Five separate samples of equal concentration were developed for varying lengths of time. The first sample was injected immediately, the second after 30 minutes, the third after 60 minutes, the fourth after 90 minutes, and the fifth after 120 minutes. The sample decay was a function of time is also shown in Figure 33. In both cases, the concentration of cyanogen chloride in the head space is dependent on the length of time in which the sample was developed. The third experiment involves the effect of real exhaust samples that have been stored over a period of time. Sample storage stability is necessary when samples cannot be processed immediately or if confusing data is to be checked at a later date. A random sample was chosen and reprocessed periodically for 50 days. The results are shown in Figure 34. As a result, samples can be stored for a period of several months without adverse effects.

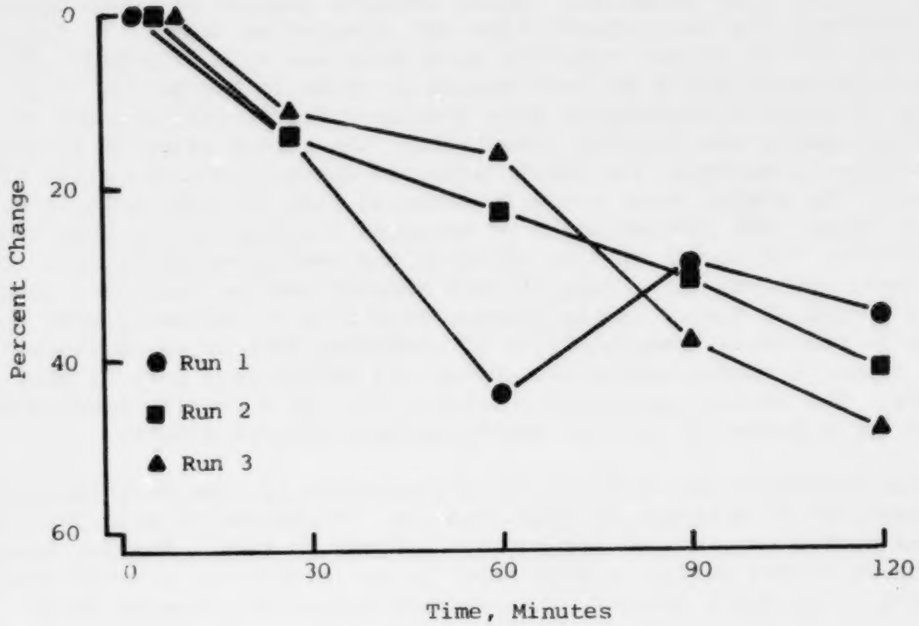
The freshness and stability of the reagents is also very important for the quantitative analysis of total cyanide. Solutions of both chloramine-T and the buffer were stored for various lengths of time. Samples developed with these stored solutions were found to be inferior to freshly prepared reagents. For these reasons, the reagents should be prepared daily.

Several ions were tested for interference with the production of cyanogen chloride or the production of other compounds with similar retention times in the column. Those ions tested were sulfate, phosphate, permanganate, nitrate, carbonate, chloride, bromide, cyanate, thiocyanate, and ammonium ions. The potassium salts of each of these ions were prepared in 100 ppm and 1 ppm concentrations in the presence of 4 ppm cyanide ion. The sulfate and nitrate salts of ammonium ion were then tried after the potassium salts of the sulfate and nitrate ions were found not to interfere. Aliquots of each were then developed for cyanogen chloride. Sulfate, phosphate, nitrate, carbonate, and ammonium ions showed no effect on the development of cyanogen chloride in the 100 ppm or 1 ppm ranges. Chloride, bromide, and permanganate ions produced little or no effect at low concentrations. At high concentrations, both bromide and permanganate ions decreased the concentration of cyanogen chloride produced. On the other hand, chloride ion increased the concentration. Cyanate and thiocyanate ions produced a positive interference at both concentrations. Apparently, these two ions also form a halide in the presence of chloramine-T with the same retention times as cyanogen chloride.

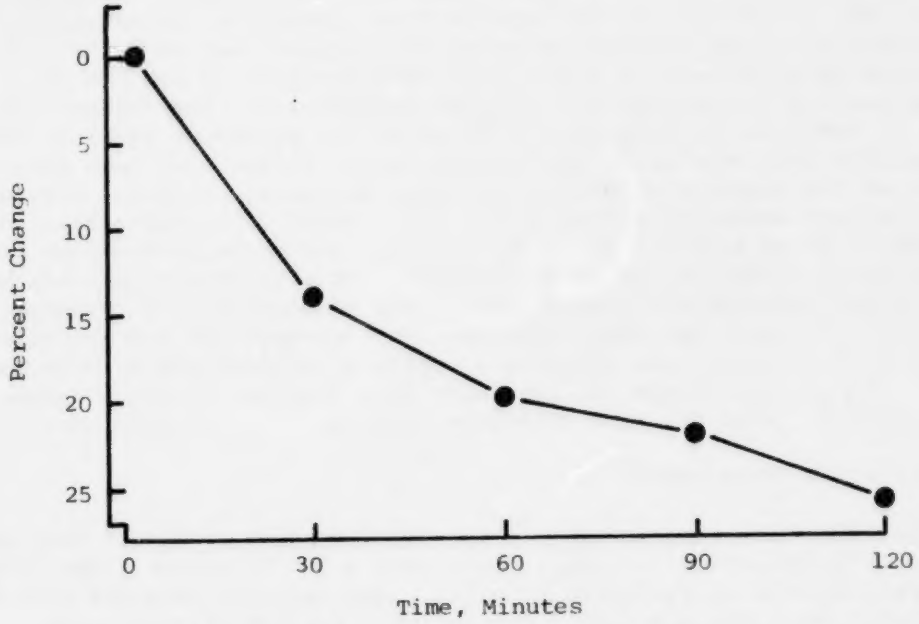
QUALIFICATION EXPERIMENTS

Qualification experiments for the total cyanide procedure were conducted with a 1978 Oldsmobile Cutlass Supreme with a 305 V8 engine. The Oldsmobile was equipped with an oxidation catalyst. The baseline emission rate for the Oldsmobile was 0.028 ppm total cyanide for a hot FTP driving cycle.

Two concentrations with a nominal concentration of 200 ppm and 500 ppm hydrogen cyanide were injected into the raw exhaust stream. Samples were passed through 1.0N potassium hydroxide absorbing reagent and were analyzed according to the gas chromatography procedure previously reported. Hydrogen



Sample decay with time



Five samples with varying development time

Figure 33. The effect of elapsed time on sample development.

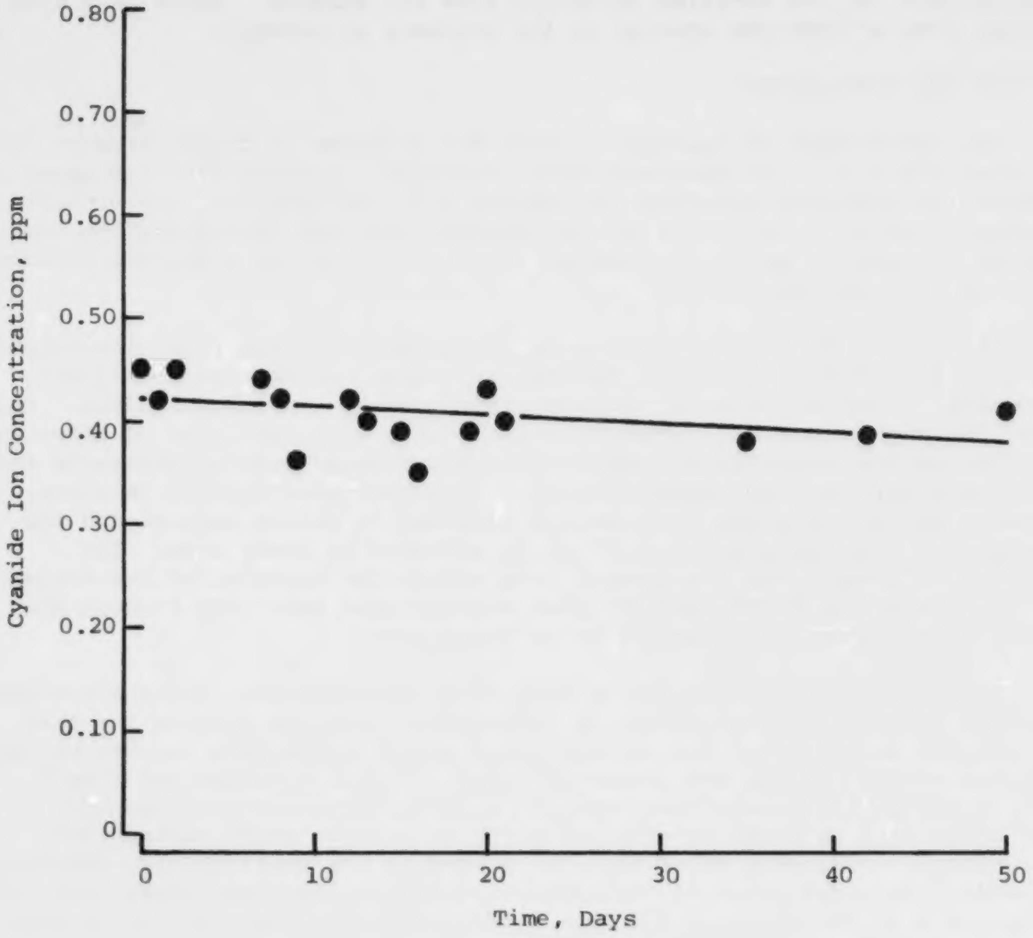


Figure 34. Time-sample decay curve.

cyanide was also injected into the CVS without exhaust. Tables 36 and 37 represent the data from these experiments.

Without exhaust, the average percent recovery for both concentrations of hydrogen cyanide is 103.0 percent. With exhaust, the average percent recovery for both concentrations is 92.9 percent. This calculation includes a correction for the baseline emissions from the exhaust. There is a 6 to 7 percent loss of hydrogen cyanide in the presence of exhaust.

RESULTS AND CONCLUSIONS

The measurement of hydrogen cyanide and cyanogen in dilute exhaust can be conducted with a gas chromatography technique. Cyanide ion is trapped in a potassium hydroxide solution and reacted with chloramine-T to produce cyanogen chloride. Injection of the cyanogen chloride determines the concentration of cyanide ion in the sample. This procedure has a minimum detection limit of 0.01 ppm cyanide ion.

The effect of interfering ions in the absorbing reagent was investigated. The ions investigated included sulfate, phosphate, permanganate, nitrate, carbonate, chloride, bromide, cyanate, thiocyanate, and ammonium ions. Sulfate, phosphate, nitrate, carbonate and ammonium ions exhibited no effect on the cyanide ion concentration while chloride, bromide, and permanganate ions interfered only at high concentrations. High concentrations of chloride, bromide, and permanganate ions are not expected in dilute exhaust and the cyanide ion concentrations should not be affected by these ions. The presence of cyanate and thiocyanate ions affect the cyanide ion concentration, and therefore, the definition of total cyanide must take into account the possible existance and interference of these ions.

As a result of preliminary testing with real exhaust, it was discovered that two bubblers were necessary to efficiently trap the cyanide ion that was present in exhaust. Two factors which might necessitate the use of two bubblers instead of one are presented below. First, cyanogen has a much lower trapping efficiency that hydrogen cyanide in potassium hydroxide. This difference in trapping efficiency was discovered while naming high concentration cylinders which were to be used in the qualification experiments. Secondly, the temperature of the exhaust stream is somewhat higher than the temperature of the gases used in the determination of the sampling parameters. The same breakthrough can be expected as with ambient conditions because the sample gas is not cooled effectively by only one impinger in the ice bath. Two impingers are therefore necessary for complete sample recovery. The final sampling parameters are listed below:

1. 25 ml of 1.0N potassium hydroxide absorbing reagent.
2. Absorbing reagent held at ice bath temperature (0°C - 5°C).
3. Sample flow rate of 4.0 ℓ/min.
4. Impingers rather than fritted glass bubblers.

TABLE 36. TOTAL CYANIDE GASEOUS RECOVERY FROM DILUTE EXHAUST BY DIRECT CVS INJECTION DURING A HOT FTP DRIVING CYCLE

			Total Cyanide Concentration as HCN, ppm			
Actual ppm Injected	Run	Sample	Calculated Amount	Observed (exhaust + air)*	Exhaust Correction	Percent Recovery
210	1	1	0.208	0.229	0.028	96.7
210	2	1	0.232	0.239	0.028	90.8
210	2	2	0.232	0.232	0.038	87.8
					Average	91.8
485	1	1	0.542	0.553	0.028	96.8
485	2	1	0.562	0.553	0.028	93.4
485	2	2	0.562	0.543	0.028	91.7
					Average	94.0

---

* Values corrected for two bubblers. Only one was used at this time.

TABLE 37. TOTAL CYANIDE GASEOUS RECOVERY BY DIRECT CVS INJECTION

Actual ppm Injected	Nominal Flow Rate, ft 3/min HCN Blend	CVS	Run	Sample	Calculated ppm HCN dilute	Observed ppm*	Percent Recovery HCN
210	0.35	350	1	1	0.213	0.214	100.4
210	0.35	350	2	1	0.208	0.226	108.5
210	0.35	350	3	1	0.218	0.225	103.0
210	0.35	350	3	2	0.218	0.227	103.9
						Average	104.0
485	0.35	350	1	1	0.471	0.472	100.1
405	0.35	350	2	1	0.493	0.465	94.3
485	0.35	350	3	1	0.510	0.561	110.0
485	0.35	350	3	2	0.510	0.528	103.5
						Average	102.0

---

* Values corrected for two bubblers. Only one was used at this time.

5. Two impingers in series.

These parameters were sufficient to collect a sample from dilute exhaust within the detection limits of the procedure.

The measurement of hydrogen cyanide in the presence of cyanogen is difficult if wet chemical techniques are used. In clear or dark Tedlar bags, hydrogen cyanide is stable for at least 60 minutes, if the humidity within the bag is not too high. High humidity increases the possibility of hydrogen cyanide condensation on the walls of the bag. Cyanogen, on the other hand, cannot be quantitively stored in the presence of exhaust. Therefore, bag samples for the measurement of cyanogen is only a qualitative tool which can determine if cyanogen is actually produced in exhaust.

Injection repeatability, sample stability, and sample storage are three basic requirements for most analytical methods. The injection repeatability is well within the expected nominal 5 percent limit for a gaseous syringe injection. The concentration of cyanogen chloride within the head space is dependent upon the volume of the head space, the room temperature, and concentration of cyanide ion present. A 5 mℓ reaction vial with a septum cap is used in the analysis. A total of 4 mℓ of the various solutions is added to this vial. When the vial is tightly capped, a 1 mℓ head space remains above the solution. This head space remains constant unless the vial is not tightly capped or the wrong volumes of reagents are pipetted into the vial. Cyanogen chloride obeys Henry's law in the head space. Henry's laws states that the mass of a slightly soluble gas that dissolves in a definite mass of a liquid at a given temperature is very nearly proportional to the partial pressure of that gas. Henry's law holds for gases which do not chemically unite with the solvent and is obeyed by a variety of gases in dilute solutions and all gaseous solutions at the limit of extreme dilution. The sample stability is maintained for only a short time after complete development. The sample must be injected five minutes after adding the reagents. After that time, the sample begins to decay and the sample integrity is not maintained. A sample may be stored undeveloped in the potassium hydroxide absorbing reagent for at least three weeks.

From the qualification experiments with hydrogen cyanide the average CVS percent recovery in exhaust is 92.9 percent. A total CVS loss of 7 percent for hydrogen cyanide is expected with dilute exhaust. Hydrogen cyanide is known to react with alkenes, alkynes, aldehydes, and ketones under the proper conditions. It also forms complexes with many metals. The apparent loss may be explained in this manner. No steps were taken to determine the specific sources of this anomalous behavior.

This procedure provides a rapid and sensitive method for the analysis of total cyanide in dilute exhaust. The analysis of a single sample requires two minutes for reagent addition, five minutes for sample development, and five minutes for the total peak elution time. Total sample processing time is twelve minutes per sample. The simplicity and ease of analysis makes this procedure ideal for repetitive analysis.

SECTION 9

ORGANIC SULFIDE PROCEDURE

LITERATURE SEARCH

The organic sulfides that are included in this analysis are carbonyl sulfide, methyl sulfide, methyl disulfide, and ethyl sulfide. The chemical formulas, molecular weights, freezing points, boiling points, and common synonyms are listed in Table 38. Carbonyl sulfide is the only sulfide of interest that is a gas at room temperature. In general, the organic sulfides are malodorous compounds that produce an unpleasant odor similar to rotten eggs. The 1968 American Conference of Governmental Industrial Hygienists made no recommendation for threshold limit values for these sulfides.

TABLE 38. LIST OF SULFUR COMPOUNDS INCLUDED IN THE ANALYSIS OF ORGANIC SULFIDES

Sulfur Compound	Chemical Formula	Molecular Weight	Freezing Point, °C	Boiling Point, °C	Synonyms
Carbonyl Sulfide	COS	60.075	-138.8	-50.2	Carbon oxysulfide
Methyl Sulfide	CH_3SCH_3	62.13	-98.27	37.3	Dimethylsulfide
Methyl Disulfide	CH_3SSCH_3	94.20	-84.72	109.7	Dimethyldisulfide
Ethyl Sulfide	$C_2H_5SC_2H_5$	90.19	-1093.9	92.1	Diethylsulfide

Several gas chromatographic methods have been used for the analysis of organic sulfides originating from a wide variety of sources. A gas chromatograph with a thermal conductivity detector has been used by several workers to analyze gas odorants for mercaptans and/or sulfides (83-87); however, none of these works were concerned with trace gas analysis. Gas chromatography and mass spectroscopy were used to separate and identify low boiling sulfur compounds in crude oil (88-90). Temperature programmed gas chromatography was found to improve the separation of mercaptans and sulfides (91-93). The separation and identification of hydrogen sulfide, sulfur dioxide, mercaptans, alkyl sulfides, and disulfides in Kraft pulp digester blow gas and black liquor combustion products was accomplished using gas chromatography (94).

Carbonyl sulfide has been quantitatively measured in natural gas (95) and in carbonated beverages (96) by the use of gas chromatography. The measurement of carbonyl sulfide in carbonated beverages used an electron capture detector and had a detector limit of 0.3 ppm. Improved sensitivity in the detection of sulfur compounds in waste process gases was accomplished by concentrating the compounds on activated silica gel at -78.5°C, desorbtion under heat and vacuum, trapping at -196°C, and transferring to gas chromatograph for analysis (97).

Several columns have been used to separate sulfur compounds from normally occurring atmospheric hydrocarbons, but little success has been obtained (98). A GC-microcoulometry method eliminated the interference from the hydrocarbons and was sensitive to 1 ppm mercaptan (99). A gas phase chemiluminescent reaction of ozone with organic sulfides has been considered as method of detection in monitoring low concentration of ozone and sulfur containing pollutants (100).

The detection limits for the analysis of sulfur compounds were improved greatly with the development of the Melpar flame photometric detector (FPD). The characterization of the FPD response to several sulfur compounds was carried out by Mizany (101). The FPD detector has been applied to low concentration air pollution monitoring (65), measurement of trace organic sulfides in air (102), and soil and water analysis (102). Permeation tubes have been used in several cases to generate continuous samples of known concentrations of various sulfur compounds (64,65). The use of Teflon throughout the gas chromatograph system has been found to minimize absorptive losses (102) and has increased sensitivity to 10 ppb (64).

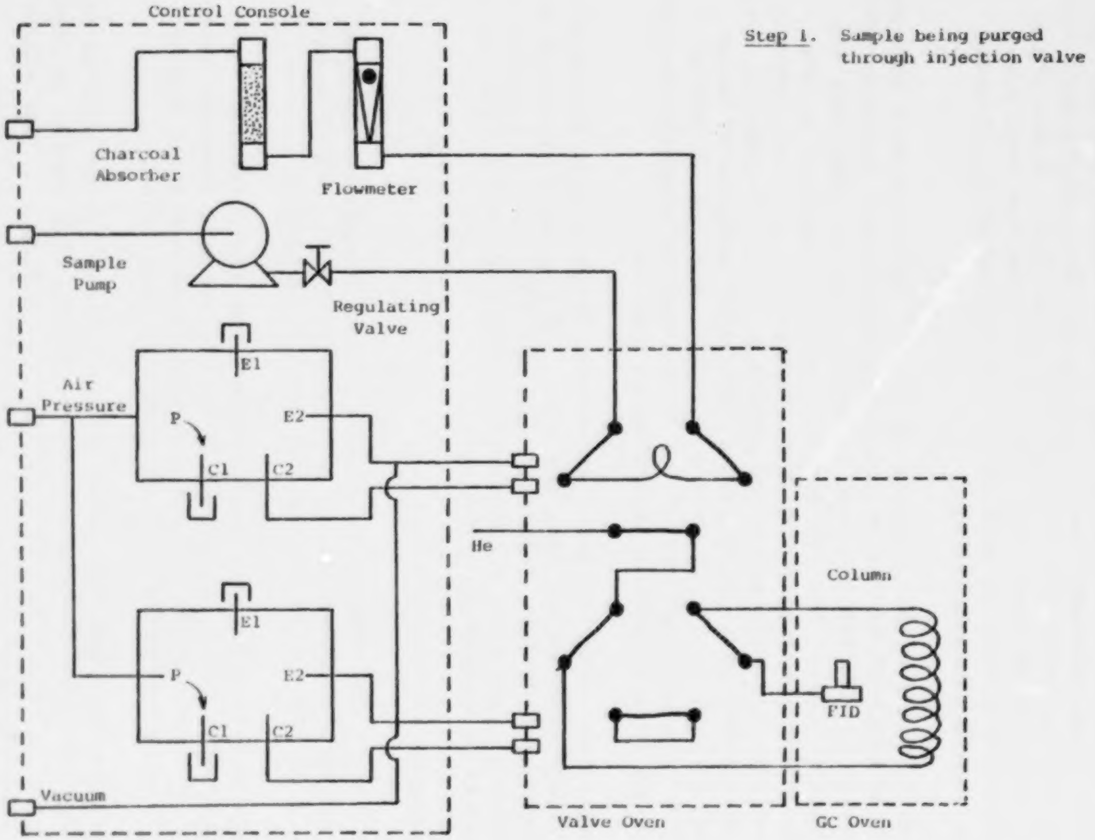
Several columns have been evaluated at several temperatures in conjunction with the Melpar flame photometric detector (70). The columns evaluated were Chromosorb T, Carbopak B-HT-100, Chromosil 310, and Deactigel. A number of other sulfur compounds have been quantitatively measured from a wide variety of sources using gas chromatography (103-109).

PROCEDURAL DEVELOPMENT

From the results of the literature search it was determined that the analysis of the organic sulfides should be conducted by the use of a gas chromatograph (GC) equipped with a flame photometric detector.

A Perkin Elmer Model 3920 B gas chromatograph was dedicated for this purpose. The instrument has a linearized flame photometric detector (FPD) and a sub-ambient oven accessory. The sub-ambient oven accessory allows for maximum flexibility in determining GC operating conditions.

A flow schematic of the gas chromatograph analytical system used in the procedural development work is shown in Figures 35-37. The sample is purged through the gas sampling valve sample loop (Figure 35 Step 1). The values are maintained isothermally at 100°C in a valve oven. The sample is injected into the gas chromatograph after the system has been efficiently purged (Figure 36 Step 2). After all peaks of interest have eluted from the analytical column, the column is backflushed and the system is readied for the next injection (Figure 37 Step 3).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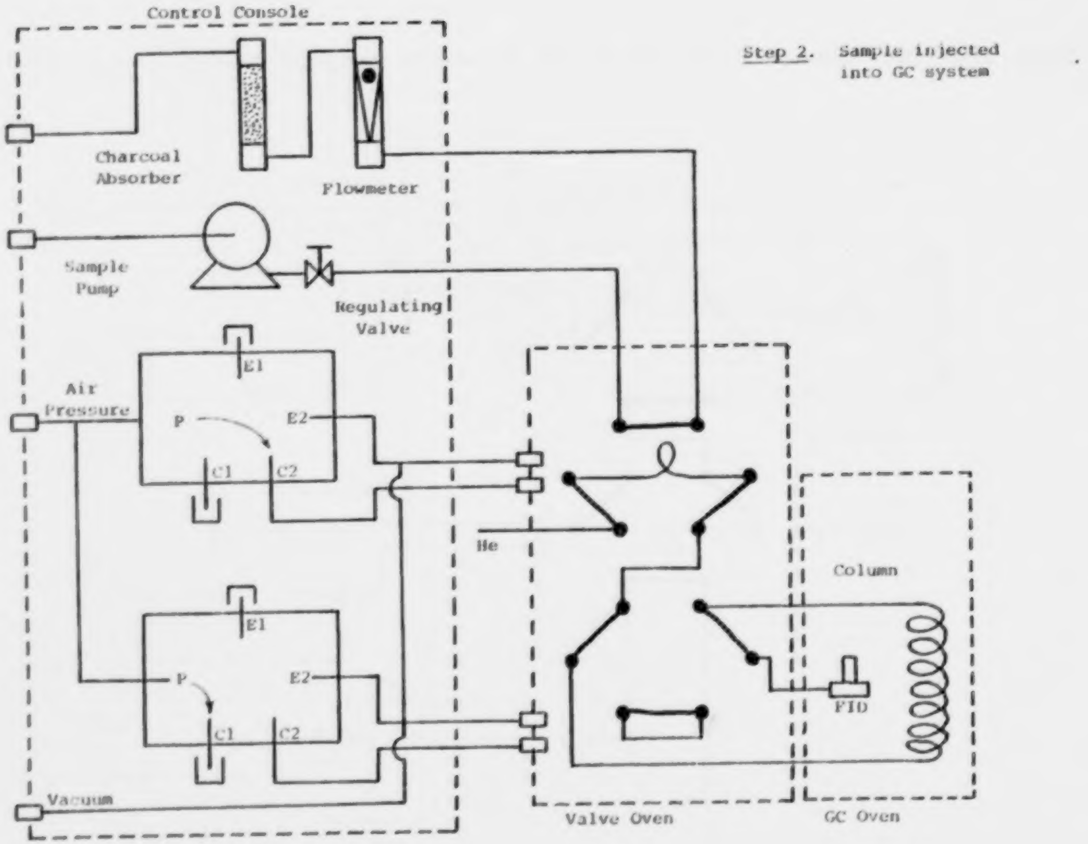
Charcoal Absorber
Flowmeter
Sample Pump
Regulating Valve
Air Pressure
Vacuum
E1
E2
P
C1
C2
E1
E2
P
C1
C2
He
Column
FID
Valve Oven
GC Oven

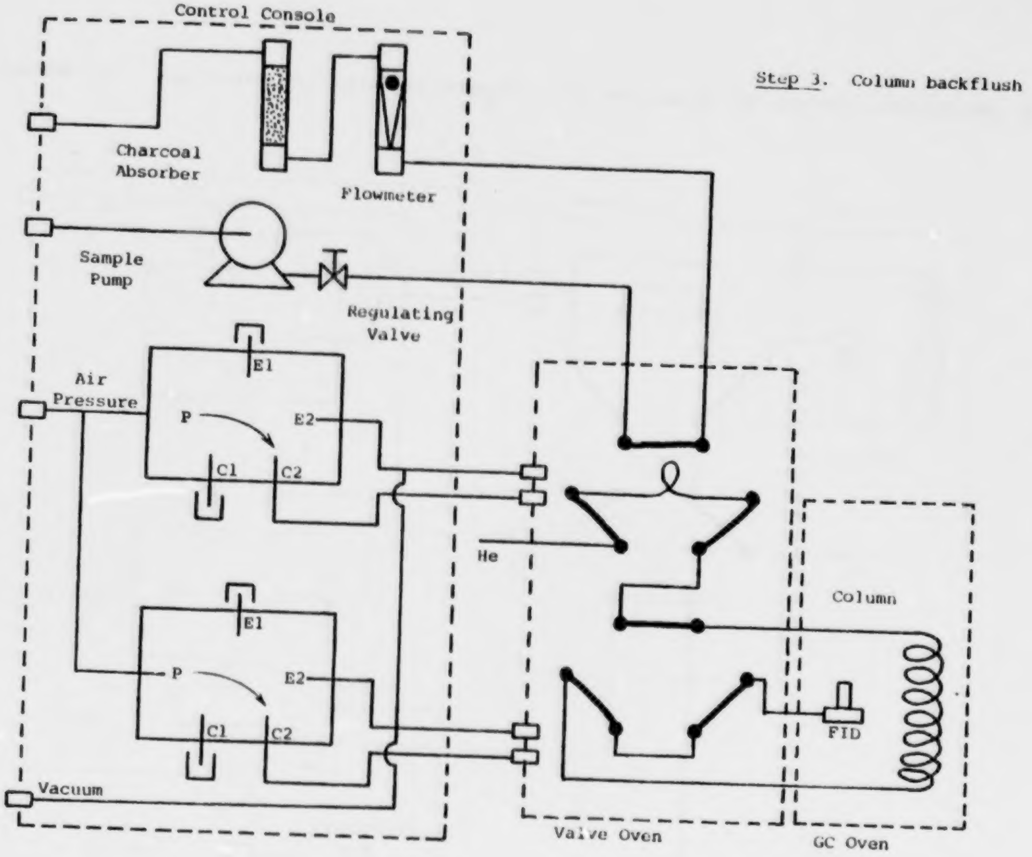
Step 1. Sample being purged through injection valve

Figure 35. Proposed GC flow schematic for analysis of organic sulfides (Step 1).


Control Console
Charcoal Absorber
Flowmeter
Sample Pump
Regulating Valve
Air Pressure
P
E1
E2
C1
C2
P
E1
E2
C1
C2
Vacuum
He
Valve Oven
Column
FID
GC Oven

Step 2. Sample injected into GC system

Figure 36. Proposed GC flow schematic for analysis of organic sulfides (Step 2).



Step 3. Column backflush

Control Console
Charcoal
Absorber
Flowmeter
Sample
Pump
Regulating
Valve
Air
Pressure
E1
P
E2
C1
C2
E1
P
E2
C1
C2
Vacuum
He
Valve Oven
Column
FID
GC Oven

Figure 37. Proposed GC flow schematic for analysis of organic sulfides (Step 3).

The column selected for the initial work was a 6' x 1/8" Teflon column packed with 60/80 Chromasil 310. Several different GC operating conditions were tried, and a preliminary set of conditions were selected that provided an adequate separation of the four organic sulfides of interest. The separation of these sulfides is presented in Figure 38. The elution of other sulfur containing compounds is also included. Table 39 presents a list of chemical and physical characteristics of various sulfur compounds that could be present in automotive exhaust.

A lecture bottle of carbonyl sulfide, pure liquids of methyl sulfide, ethyl sulfide, and methyl disulfide, along with a Tracor Model 412 Permeation Calibration System containing all four sulfides, were used as sources for the organic sulfides in the procedural development. Permeation tubes of methyl mercaptan, ethyl mercaptan, hydrogen sulfide, and sulfur dioxide, blends of hydrogen sulfide and sulfur dioxide in aluminum cylinders with balance nitrogen, lecture bottles of hydrogen sulfide, sulfur dioxide, and methyl mercaptan, and a pure liquid of ethyl mercaptan were used in the interference checks.

Two methods of sample acquisition were considered for the analysis of the organic sulfides. One method would be to use sample bags obtained during the standard CVS testing. An alternate approach would be to use a trap packed with a material such as Tenax GC for concentrating the sample. In this manner an exhaust sample would be pulled through the trap during the entire test, thereby giving an effective sample volume of several liters rather than 5-10 mℓ. The use of the trap would increase the limits of detectability by a factor of over 1000. The collection by the use of sample bags was discarded due to the expected low concentrations of organic sulfides in exhaust and the large losses of methyl sulfide, ethyl sulfide, and methyl disulfide onto the walls of the Tedlar bags at ppb levels. Because the concentration of the organic sulfides is expected to be very low in exhaust, a number of experiments were conducted to investigate various concentration techniques that may apply to the measurement of the organic sulfides.

The first set of experiments involved the use of a U-tube type trap and was conducted using several trap volumes ranging in size from 5 to 20 mℓ. The basic flow schematic of the sampling system is shown in Figure 39. A permeation gas blend of carbonyl sulfide and methyl sulfide was used in these experiments, with the actual concentration depending on the particular experiment. Two flow rates through the traps were used: 12.0 mℓ/min (9.50 ppm COS and 4.77 ppm CH_3SCH_3) and 81.2 mℓ/min (1.40 ppm COS and 0.71 ppm CH_3SCH_3). The traps were maintained at -78°C during the sampling period. The purpose of these experiments was to see if it is possible to cold trap (at -78°C) the sulfides and then use the cold trap as a sample loop on the gas chromatograph system. Results of these experiments are presented in Table 40. Based on these results, it was apparent that the carbonyl sulfide and methyl sulfide could not both be retained under any of the trap sizes or concentrations investigated. The only condition that indicated there may be some possibility for this method was the large trap loop (20 mℓ) at the higher flow rate and lower concentration. Even

GAS CHROMATOGRAPH CONDITIONS

Perkin-Elmer 3920B w/FPD 6' x 1/8" column packed with 60/80 chromasil 310, N_2 at 20 mℓ/min., oven iso at 0°C for 8 min and programmed to 140°C/min. at 32°C/min.

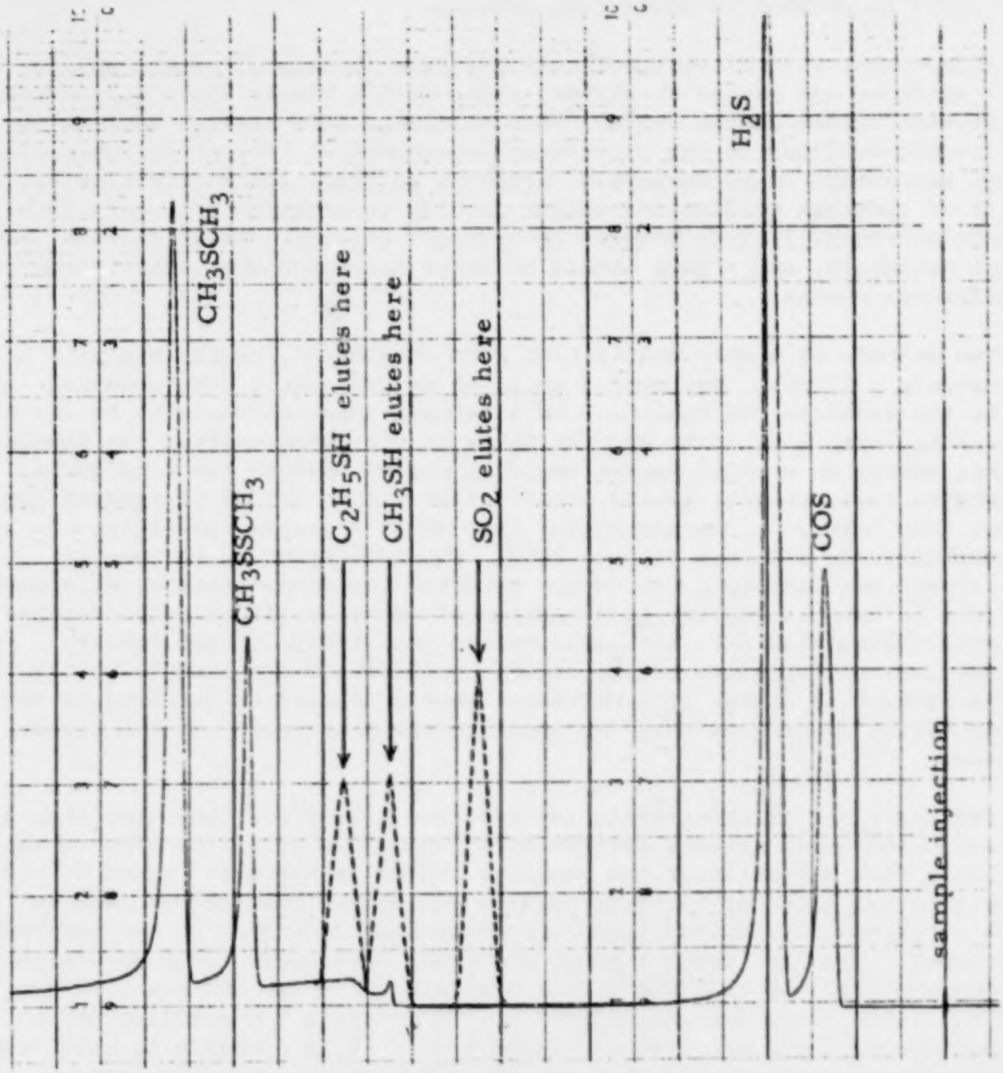


Figure 38. Gas chromatograph separation of several organic sulfides in prepared blend.

TABLE 39. LIST OF CHEMICAL AND PHYSICAL CHARACTERISTICS OF VARIOUS SULFUR COMPOUNDS POTENTIALLY PRESENT IN AUTOMOTIVE EXHAUST

Sulfur Compound	Chemical Formula	Molecular Weight	Density	Boiling Point, °C	Retention Time
Carbonyl Sulfide	COS	60.075	2.5300 g/ℓ	-50.2	2.8
Hydrogen Sulfide	H_2S	34.08	1.5392 g/ℓ	-60.3	4.2
Sulfur Dioxide	SO_2	64.063	2.927 g/ℓ	-10.0	10.5
Dimethyl Sulfide	CH_3SCH_3	62.13	0.848 g/mℓ	37.3	17.5
Dimethyl Disulfide	CH_3SSCH_3	94.20	1.0625 g/mℓ	109.7	15.8
Diethyl Sulfide	$C_2H_2SC_2H$	90.19	0.836 g/mℓ	92.1	----
Methyl Mercaptan	CH_3SH	48.11	0.8665 g/mℓ	6.2	12.5
Ethyl Mercaptan	C_2H_5SH	62.13	0.8391 g/mℓ	35	13.5

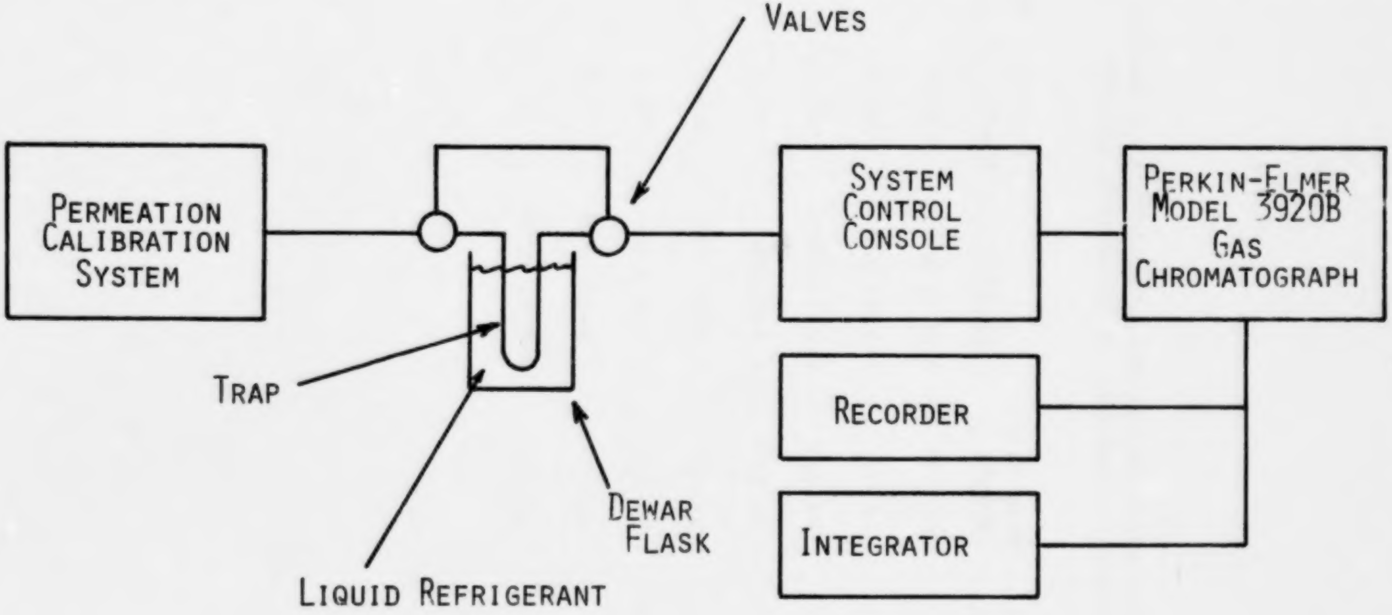

Valves
Permeation Calibration System
System Control Console
Perkin-Elmer Model 3920B Gas Chromatograph
Trap
Recorder
Dewar Flask
Integrator
Liquid Refrigerant

Figure 39. Cold trap experiment flow schematic.

TABLE 40. THE EFFECT OF COLD TRAPPING AT -78°C ON CARBONYL SULFIDE AND METHYL SULFIDE AT VARIOUS CONCENTRATIONS, FLOW RATES AND TRAP SIZES

Trap loop, mℓ	Trap Flow mℓ/min	inj.	Trap Inlet Conc., ppm COS	Trap Inlet Conc., ppm CH_3SCH_3	Trap Inlet Peak Height COS	Trap Inlet Peak Height CH_3SCH_3	Trap Exit Peak Height COS	Trap Exit Peak Height CH_3SCH_3
5.0	12.0	1	9.50	4.77	84.5	16.1	84.2	4.1
5.0	12.0	2	9.50	4.77	84.5	16.0	84.2	13.8
				Avg.	84.5	16.0	84.2	9.0
10.0	12.0	1	9.50	4.77	84.2	13.3	84.5	1.1
10.0	12.0	2	9.50	4.77	84.2	13.4	84.5	11.4
				Avg.	84.2	13.4	84.5	6.3
15.0	12.0	1	9.50	4.77	84.2	13.3	84.9	12.6
15.0	12.0	2	9.50	4.77	84.2	13.4	84.9	13.0
				Avg.	84.2	13.4	84.9	12.8
20.0	12.0	1	9.50	4.77	85.0	14.6	84.9	0.0
20.0	12.0	2	9.50	4.77	85.0	14.4	84.9	10.0
				Avg.	85.0	14.5	84.9	5.0
5.0	81.2	1	1.40	0.71	63.0	5.2	64.9	5.2
5.0	81.2	2	1.40	0.71	63.5	5.2	65.0	4.2
				Avg.	63.2	5.2	65.0	4.7
10.0	81.2	1	1.40	0.71	63.0	5.2	63.0	4.2
10.0	81.2	2	1.40	0.71	63.5	5.2	63.5	4.2
				Avg.	63.2	5.2	63.2	4.2
15.0	81.2	1	1.40	0.71	63.0	5.2	62.0	5.0
15.0	81.2	2	1.40	0.71	63.5	5.2	62.1	4.5
				Avg.	63.2	5.2	62.1	4.8
20.0	81.2	1	1.40	0.71	63.0	5.5	65.0	0.0
20.0	81.2	2	1.40	0.71	62.0	5.0	66.0	0.0
				Avg.	62.5	5.3	65.5	0.0

in this particular case, the trapping was effective only on methyl sulfide.

One additional trap temperature was investigated prior to elimination of cold trapping as a possible concentration technique. In this experiment the trap was cooled to liquid nitrogen temperature. The results of this experiment are presented in Table 41. Only one set of concentrations (1.40 ppm COS and 0.71 ppm CH_3SCH_3) was used in this experiment. All sample loop sizes were somewhat effective in collecting the carbonyl sulfide, with a nominal collection efficiency ranging from 76 to 86 percent. The collection efficiency for methyl sulfide was slightly higher, but the repeatability was less, probably due to the low peak heights for this species. From these experiments it was apparent that cold trapping, using traps up to 20 mℓ in volume, and temperatures as low as -196°C would not quantitatively remove either carbonyl sulfide or methyl sulfide.

Efforts were then directed toward determining the feasibility of using short stainless steel cartridges packed with an absorbing material to concentrate the organic sulfides. The absorption traps are lengths of stainless steel tubing 2 inches in length and 3/8" OD. The material is held in the stainless cartridge by stainless micron inserts in each of the unions on both ends. Four packing materials were selected to be evaluated at four collection temperatures. The four packing materials that were used in this experiment include Tenax-GC, Chromosorb 102, Poropak Q, and Chromosorb T. The collection efficiency of these traps was evaluated at temperatures of 20°C, 0°C, -78°C, and -196°C.

A permeation calibration gas sample containing 1.40 ppm carbonyl sulfide and 0.71 ppm methyl sulfide in a balance nitrogen gas was used for this study. The results of this study are presented in Table 42. Three of the four packings are essentially 100 percent efficient in removing both carbonyl sulfide and methyl sulfide at -78°C. These three packings were Tenax-GC, Chromosorb 102, and Poropak Q. All of the traps except Chromosorb T were effective in removing methyl sulfide at all of the temperatures investigated. Problems were encountered using trap temperatures of -196°C. At this temperature flow, restrictions were noted in the trap as the test proceeded. There were also problems in desorbing traps that were stored at this temperature.

The sulfides were thermally desorbed from the traps by connecting the traps into the gas injection system with two quick connects and immediately injecting the sample into the GC system and placing the traps inside a Lindburg furnace operating at 300°C. The carrier gas upon injection flows through the loop carrying the contents of the trap into the gas chromatograph. The 300°C temperature is the temperature needed to thermally desorb the traps without causing broad sulfide peaks which result from gradual thermal desorbtion. The 300°C temperature is also low enough to prevent the destruction of the packing material in the trap. The packing material which gave the most reproducible results in the desorbtion experiments was Tenax GC. For this this reason and its stability at the 300°C desorbtion temperature, the Tenax GC packing material was selected for use in subsequent experiments.

TABLE 41. THE EFFECT OF COLD TRAPPING AT -196°C ON CARBONYL SULFIDE AND METHYL SULFIDE WITH VARIOUS TRAP SIZES

	Trap		Trap Inlet				Trap Exit	
Trap	Flow		Conc.,ppm		Peak Height		Peak Height	
loop, mℓ	mℓ/min	inj.	COS	CH_3SCH_3	COS	CH_3SCH_3	COS	CH_3SCH_3
5.0	81.2	1	1.40	0.71	66.7	5.3	15.8	0.8
5.0	81.2	2	1.40	0.71	66.7	5.3	15.8	0.1
		Avg.	1.40	0.71	66.7	5.3	15.8	0.5
10.0	81.2	1	1.40	0.71	67.8	5.2	16.0	0.0
10.0	81.2	2	1.40	0.71	68.1	5.2	15.2	0.0
		Avg.	1.40	0.71	68.0	5.2	15.6	0.0
15.0	81.2	1	1.40	0.71	67.8	5.2	8.0	0.1
15.0	81.2	2	1.40	0.71	68.1	5.2	10.8	0.1
		Avg.	1.40	0.71	68.0	5.2	9.4	0.1
20.0	81.2	1	1.40	0.71	78.0	5.5	8.0	0.0
20.0	81.2	2	1.40	0.71	78.9	5.5	14.0	0.1
		Avg.	1.40	0.71	78.5	5.5	11.0	0.05

TABLE 42. THE EFFICIENCY OF VARIOUS MATERIALS TRAPPING SULFIDES AT SEVERAL TEMPERATURES

			Gas Chromatograph Response-Peak Ht.			
			Before		After	
Inj.	Trap Temp.°C	Trap	COS	CH_3SCH_3	COS	CH_3SCH_3
1	20	Tenax-GC	68.2	4.2	64.5	0.0
2	20	Tenax-GC	69.5	5.3	67.5	0.0
Avg.	20	Tenax-GC	68.9	4.8	66.0	0.0
1	0	Tenax-GC	65.0	4.5	64.5	0.0
2	0	Tenax-GC	63.5	4.7	62.0	0.0
Avg.	0	Tenax-GC	64.3	4.6	63.3	0.0
1	-76	Tenax-GC	64.8	5.0	0.0	0.0
2	-76	Tenax-GC	65.0	5.0	0.0	0.0
Avg.	-76	Tenax-GC	64.9	5.0	0.0	0.0
1	20	Chromosorb 102	68.2	4.2	66.5	0.0
2	20	Chromosorb 102	69.5	5.3	68.0	0.0
Avg.	20	Chromosorb 102	68.9	4.8	67.3	0.0
1	0	Chromosorb 102	64.0	4.9	20.8	0.0
2	0	Chromosorb 102	64.2	4.3	20.0	0.0
Avg.	0	Chromosorb 102	64.1	4.6	20.4	0.0
1	-76	Chromosorb 102	67.2	4.8	0.0	0.0
2	-76	Chromosorb 102	67.2	4.8	0.0	0.0
Avg.	-76	Chromosorb 102	67.2	4.8	0.0	0.0
1	20	Poropak Q	62.0	5.0	63.2	0.0
2	20	Poropak Q	63.6	5.0	62.6	0.0
Avg.	20	Poropak Q	62.8	5.0	62.9	0.0
1	0	Poropak Q	64.0	4.9	35.5	0.0
2	0	Poropak Q	64.2	4.3	45.0	0.0
Avg.	0	Poropak Q	64.1	4.6	40.3	0.0
1	-76	Poropak Q	67.2	4.7	0.0	0.0
2	-76	Poropak Q	67.2	4.5	0.0	0.0
Avg.	-76	Poropak Q	67.2	4.6	0.0	0.0
1	20	Chromosorb T	65.0	4.5	64.8	3.9
2	20	Chromosorb T	63.5	4.5	65.1	4.5
Avg	20	Chromosorb T	64.3	4.5	65.0	4.2
1	0	Chromosorb T	64.8	5.0	64.0	5.0
2	0	Chromosorb T	65.0	3.9	63.2	5.0
Avg	0	Chromosorb T	64.9	4.5	63.6	5.0
1	-76	Chromosorb T	64.0	4.8	62.5	3.0
2	-76	Chromosorb T	63.0	4.8	61.0	0.0
Avg.	-76	Chromosorb T	63.5	4.8	61.8	1.5

---

[a] Trap size 2" x 3/8 OD

A Tenax trap at -76°C was used to collect the exhaust from a 1975 Model 350 CID Chevrolet engine for the 31 minutes of an FTP. The resulting trap was thermally desorbed into the GC analytical system. The gas chromatograph trace obtained from the desorbtion of the trap indicated that a substantial number of sulfur containing compounds were present. The major drawback observed was the exceptionally large sulfur dioxide (SO_2) peak.

The concentration of sulfur dioxide in the dilute exhaust will normally range from 2 to 5 ppm, whereas the other sulfides are present only in the ppb range. The sulfur dioxide is unstable and the proposed method is not designed to quantitatively measure sulfur dioxide. Since sulfur dioxide has no quantitative interest, efforts were directed to determine if techniques are available that would allow sulfur dioxide removal without altering the concentration of other sulfides. A packing material containing sodium bicarbonate ($NaHCO_3$) has been reported to be very effective for this purpose.

Experiments have indicated that hydrogen sulfide (H_2S) was not stable enough to quantify with this procedure. In order to remove the interference from sulfur dioxide and to remove any remaining hydrogen sulfide, the dilute exhaust is passed through a 2" x 3/8" stainless steel cartridge packed with 5 percent sodium bicarbonate on 45/60 mesh Chromosorb P-AW DMC before entering the organic sulfide collecting Tenax GC trap. The sodium bicarbonate trap effectively removes sulfur dioxide at 10 ppm levels and hydrogen sulfide at 1 ppm levels without affecting the organic sulfide concentrations.

Initially, a set of gas chromatograph operating parameters was developed to provide separation of hydrogen sulfide, carbonyl sulfide, sulfur dioxide, methyl mercaptan, methyl sulfide, methyl disulfide, and ethyl sulfide. Since hydrogen sulfide and sulfur dioxide are not of quantitative interest, the original GC operating parameters were modified to shorten the analysis time. The initial GC oven temperature of 0°C was maintained for four minutes and then temperature programmed to 140°C at 32°C/minute. The entire analysis time was about 25 minutes. Operation at 0°C was originally selected to allow separation of hydrogen sulfide and carbonyl sulfide. Since this separation would no longer be necessary, the GC oven parameters were changed to provide a compromise between separation and analysis time. This new programming rate provides for sample injection at 80°C followed by immediate programming to 140°C at 16°C/minute. A typical trace of the organic sulfides is shown in Figure 40.

Several recovery experiments were conducted using the Tenax GC traps. These experiments were designed to determine the recovery of the organic sulfides from the Tenax GC traps. The recovery from these traps was very erratic and was not satisfactory. Initially, it was felt that the lack of reproducibility was due to the technique employed to remove the organic sulfides from the Tenax GC traps. However, the GC analytical column was later found to be suspect. Contact was made with those researchers who originally used the GC parameters to quantitatively measure organic sulfides. Their findings were similar to those experienced at SwRI. When using this column packing near its maximum operating temperature, very erratic results were experienced. After looking into this more thoroughly, it was decided to use a different column packing that would be reproducible and still yield

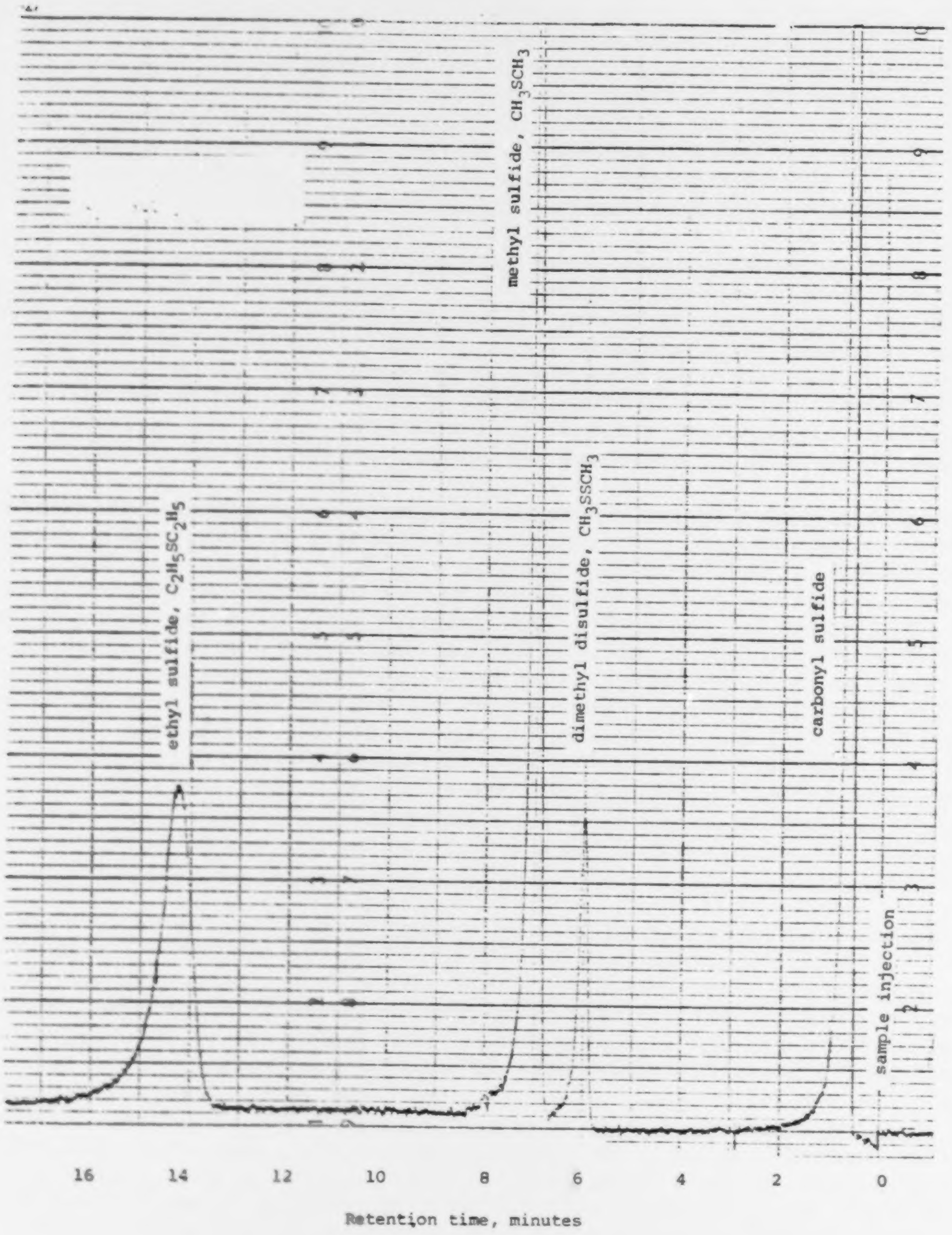


Figure 40. Typical gas chromatograph trace of organic sulfides.

satisfactory separation of the organic sulfides.

The column packing that was selected was a specially treated Porapak QS. Although this column is reported to be stable at higher temperatures, the separation characteristics are not as good as the Chromosil 310 column. The ethyl sulfide and methyl disulfide elute together. A typical calibration blend from a permeation system is presented in Figure 41. This column was also found to give inconsistent results after repeated use and a different analytical column was sought for use in measuring the organic sulfides. After reviewing the literature and conducting a brief cursory laboratory study, it was found that the column which has the necessary qualifications for the organic sulfide analysis is a 6' x 1/8" TFE Teflon column packed with 60/80 mesh Tenax GC. A typical gas chromatograph trace using the Tenax GC analytical column for the analysis of the four organic sulfide is shown in Figure 42.

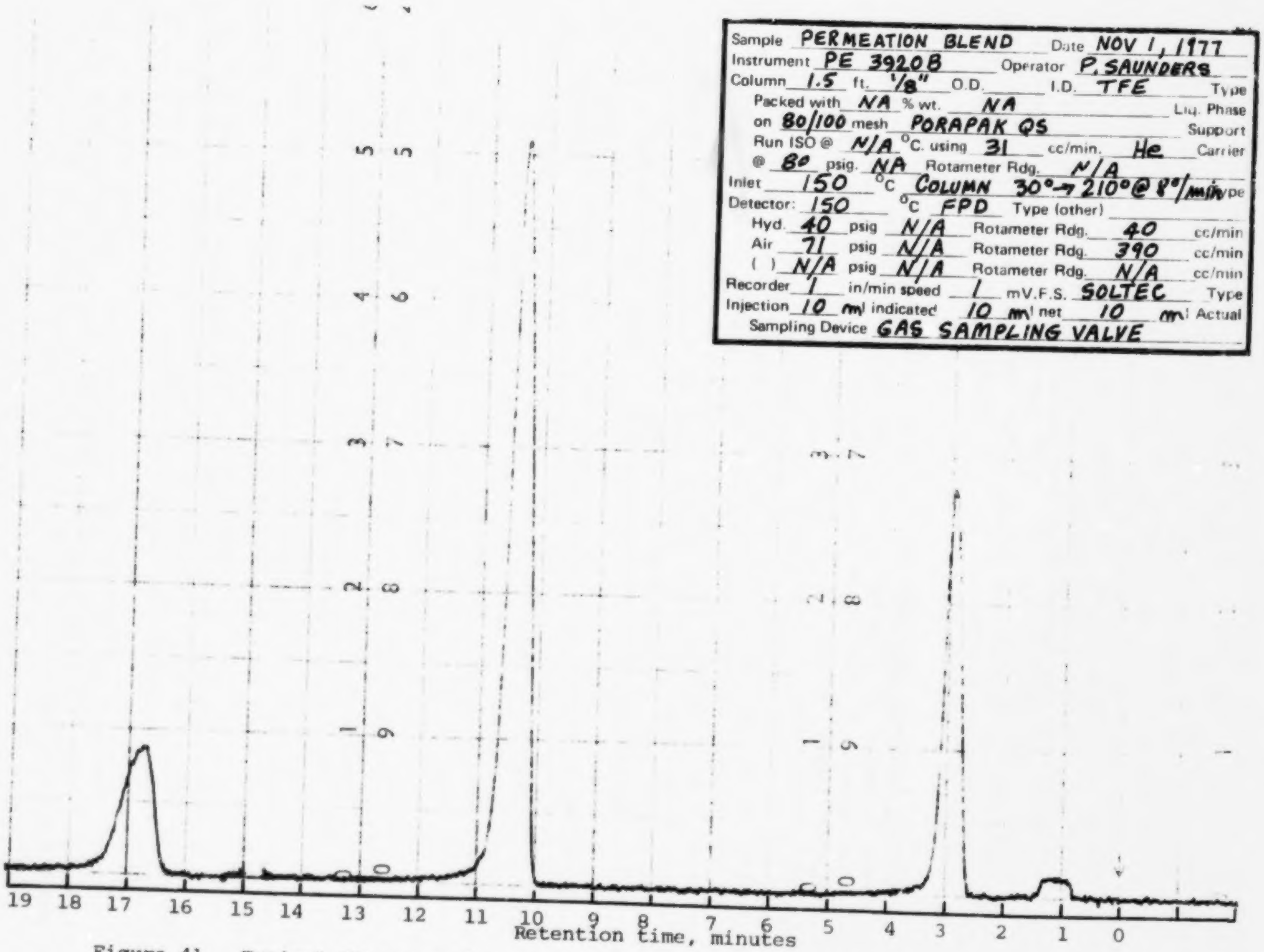
In order to determine the efficiency of the collection on Tenax GC absorbing traps, a secondary dilution of the permeation calibration system was included. The organic sulfides were diluted from a 0.1 - 3 ppm level down to the detection limits of the FPD. A sample of the permeation blend after secondary dilution is presented in Figure 43. As noted, only two of the four peaks are above the detection limits, although all four organic sulfides and the concentrations are listed at their elution time. The concentration of the organic sulfides with Tenax-GC traps appears to have tremendous potential. An example of the permeation calibration blend (with secondary dilution) after being sampled at a flow rate of 45 mℓ/min for 10 minutes is shown in Figure 44. Only the four individual organic sulfides are observed, and no extraneous peaks (reaction products, etc.) are observed.

A system was developed to re-condition the Tenax GC traps by purging the traps with nitrogen at 500 mℓ/min for seven minutes at 300°C. Several spot checks of traps that had been conditioned under these conditions indicated no trace of organic sulfide carry-over from "used" Tenax-GC traps. The procedure that is used to desorb the organic sulfides from the traps is also very efficient in that no organic sulfides are retained in the trap after the thermal desorption using the GC procedure.

The Tenax GC traps have been found to effectively remove 100 percent of the organic sulfides from a permeation calibration flow at a flow rate of 130 mℓ/min when the trap is maintained at -76°C. Higher flow rates were tried, and a breakthrough into a back-up Tenax-GC trap was observed at a flow rate of 250 mℓ/min. When this occurred, it was decided to return to 130 mℓ/min and use this flow rate as the primary sampling flow rate.

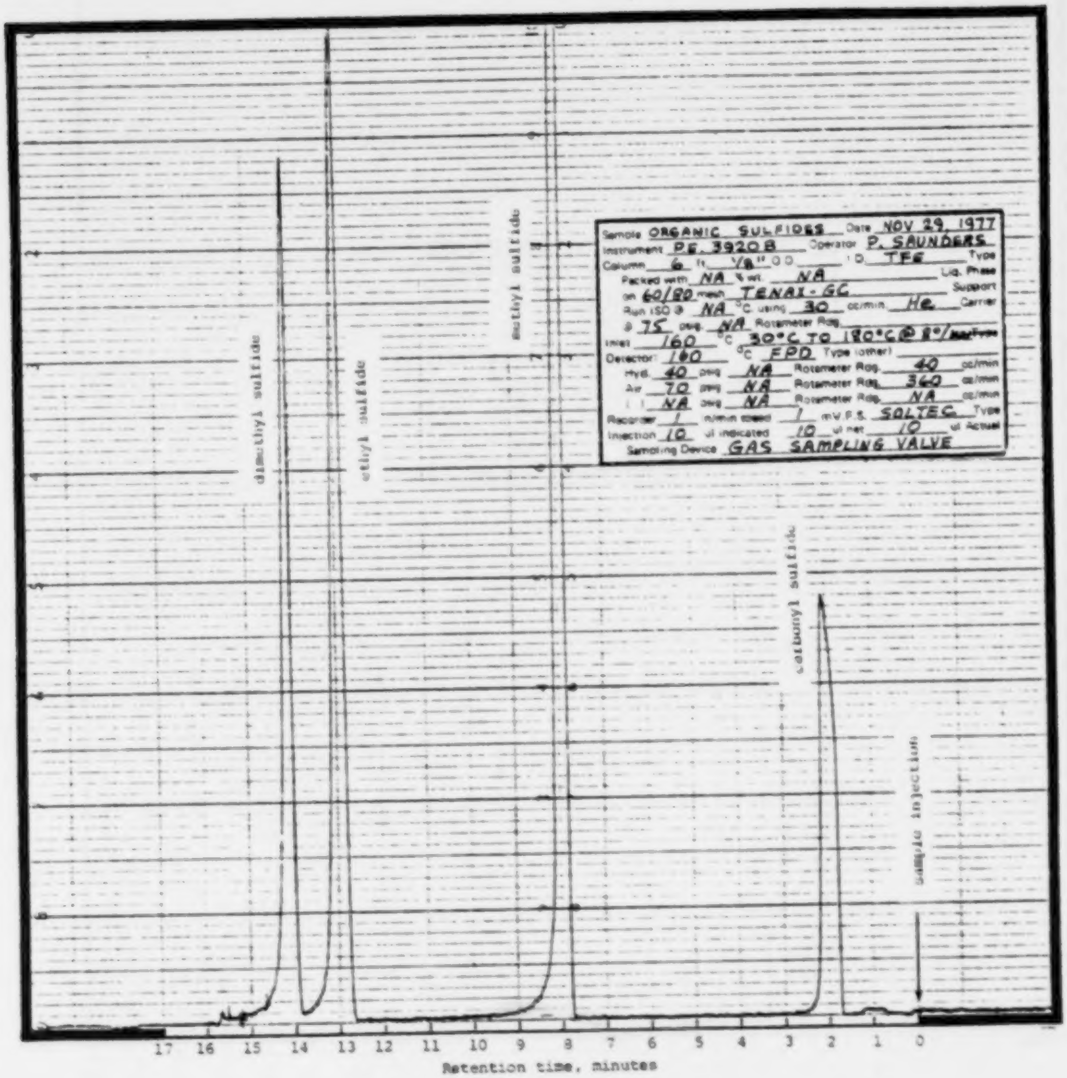
A variety of other trap designs, temperatures, and flow rates may be equally acceptable; but for the purpose of developing a procedure with specific goals, these conditions have been selected.

Problems have been encountered with batch to batch variation in the Tenax-GC which have caused repeatability problems. A procedure has been implemented to validate each Tenax-GC batch prior to sampling as well as each individual trap.



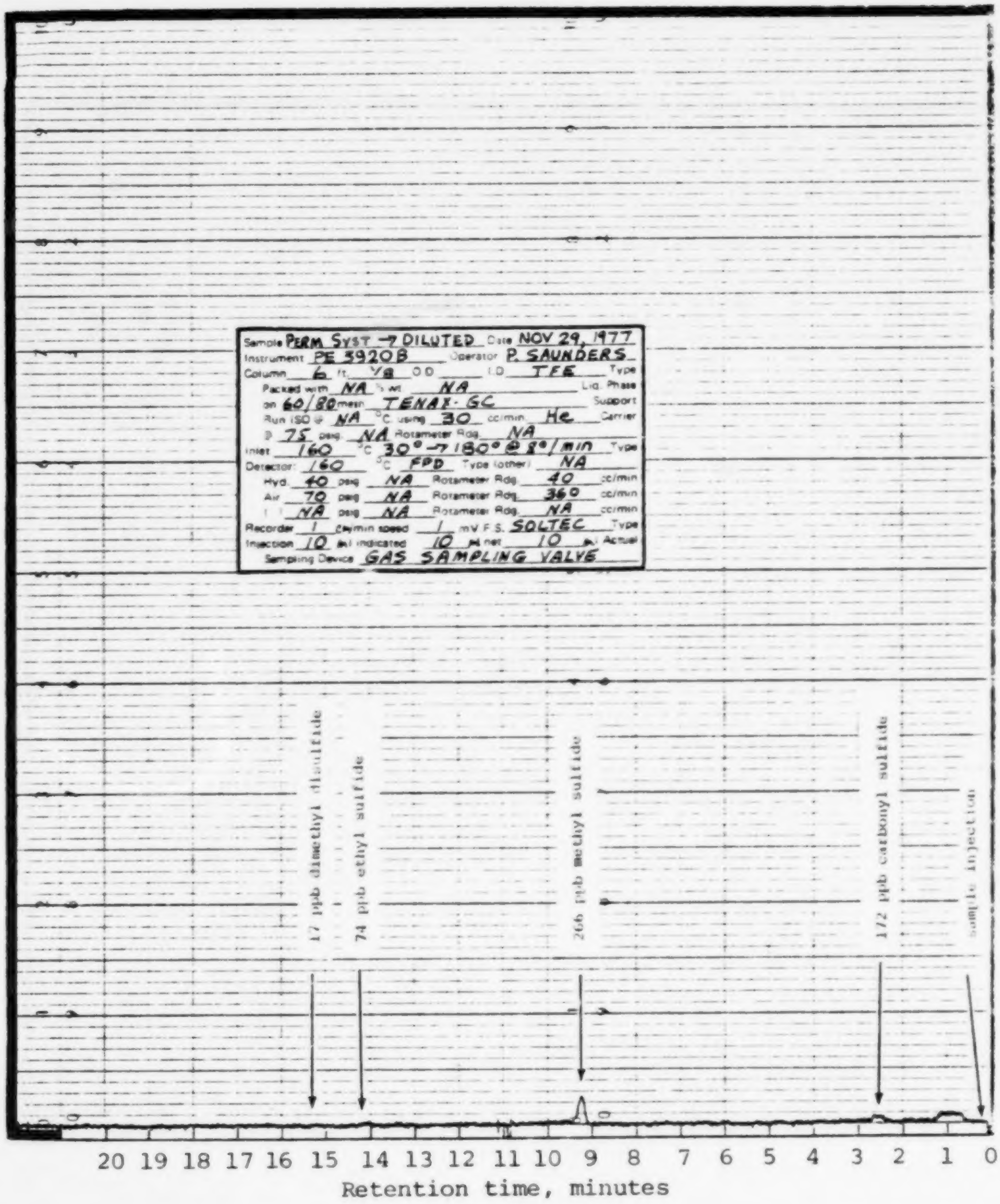
Sample PERMEATION BLEND Date NOV 1, 1977
Instrument PE 3920B Operator P. SAUNDERS
Column 1.5 ft. 1/8" O.D. ____ I.D. TFE Type
Packed with NA % wt. NA Liq. Phase
on 80/100 mesh PORAPAK QS Support
Run ISO @ N/A °C. using 31 cc/min. He Carrier
@ 80 psig. NA Rotameter Rdg. N/A
Inlet 150 °C COLUMN 30° → 210° @ 8°/min ype
Detector: 150 °C FPD Type (other) ____
Hyd. 40 psig N/A Rotameter Rdg. 40 cc/min
Air 71 psig N/A Rotameter Rdg. 390 cc/min
( ) N/A psig N/A Rotameter Rdg. N/A cc/min
Recorder 1 in/min speed 1 mV.F.S. SOLTEC Type
Injection 10 ml indicated 10 ml net 10 ml Actual
Sampling Device GAS SAMPLING VALVE

Figure 41. Typical GC separation of organic sulfides on acetone-washed Poropak QS column.



Sample ORGANIC SULFIDES Date NOV 29, 1977
Instrument PE 3920 B Operator P. SAUNDERS
Column 6 ft 1/8" OD ID TFE Type
Packed with NA % wt. NA Liq. Phase
on 60/80 mesh TENAX-GC Support
Run ISO @ NA °C using 30 cc/min He Carrier
@ 75 psig NA Rotameter Rdg
Inlet 160 °C 30°C TO 180°C @ 8°/min Type
Detector 160 °C FPD Type (other)
Hyd. 40 psig NA Rotameter Rdg. 40 cc/min
Air 70 psig NA Rotameter Rdg. 360 cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 in/min speed 1 mV F.S. SOLTEC Type
Injection 10 ul indicated 10 ul net 10 ul Actual
Sampling Device GAS SAMPLING VALVE

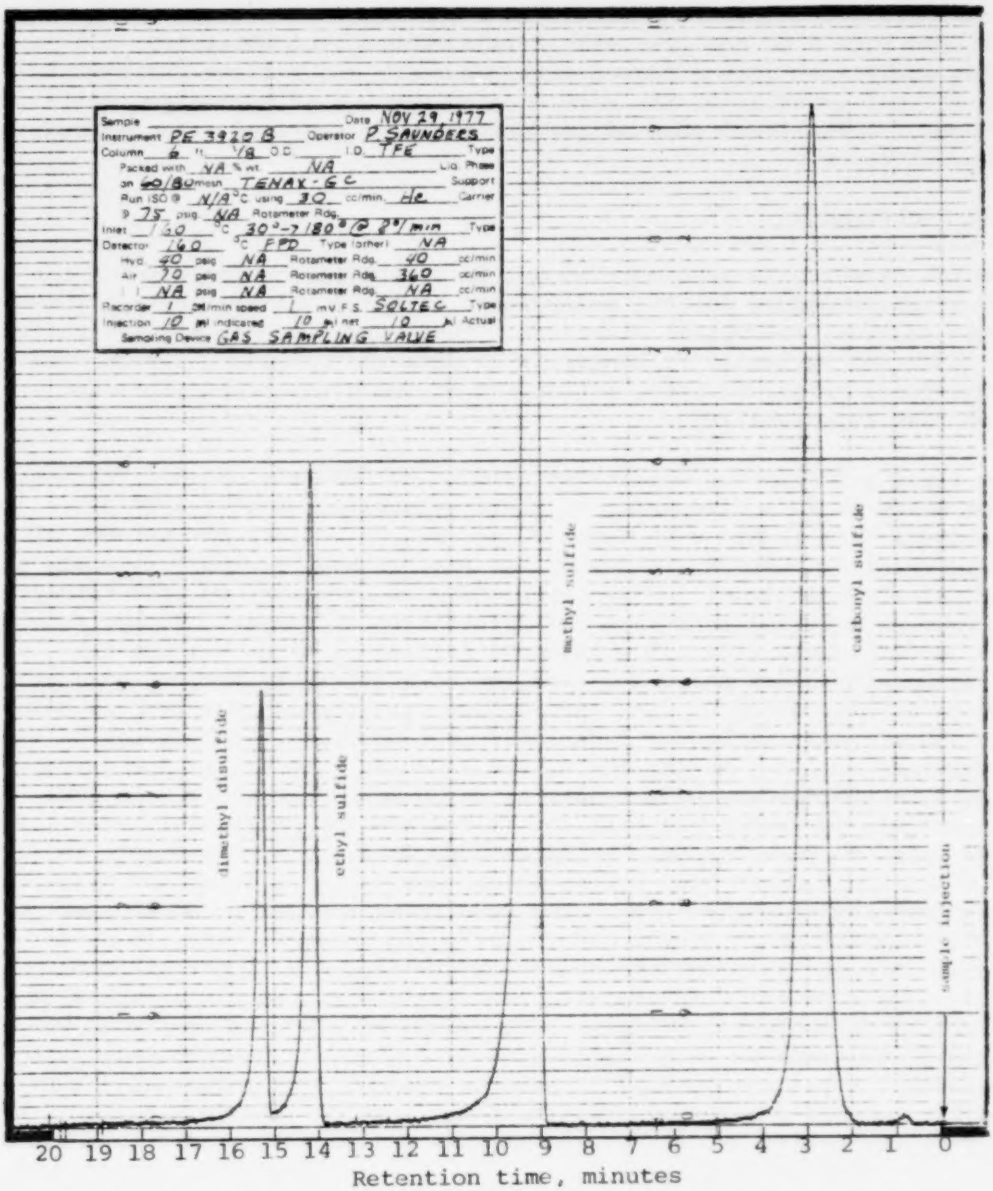
Figure 42. Typical organic sulfide separation with Tenax-GC column.



Sample PERM SYST → DILUTED Date NOV 29, 1977
Instrument PE 3920B Operator P. SAUNDERS
Column 6 ft. 1/8 O.D. I.D. TFE Type
Packed with NA % wt NA Liq. Phase
on 60/80 mesh TENAX-GC Support
Run ISO @ NA °C using 30 cc/min He Carrier
@ 75 psig NA Rotameter Rdg NA
Inlet 160 °C 30° → 180° @ 8°/min Type
Detector 160 °C FPD Type (other) NA
Hyd. 40 psig NA Rotameter Rdg 40 cc/min
Air 70 psig NA Rotameter Rdg 360 cc/min
( ) NA psig NA Rotameter Rdg NA cc/min
Recorder 1 cm/min speed 1 mV F.S. SOLTEC Type
Injection 10 µl indicated 10 µl net 10 µl Actual
Sampling Device GAS SAMPLING VALVE

17 ppb dimethyl disulfide
74 ppb ethyl sulfide
266 ppb methyl sulfide
172 ppb carbonyl sulfide
sample injection
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
Retention time, minutes

Figure 43. Organic sulfide permeation blend with secondary dilution, near detection limit of GC FPD system.



Sample ______ Date NOV 29 1977
Instrument PE 3920 B Operator P. SAUNDERS
Column 6 ft 1/8 O.D. ______ I.D. TFE Type
Packed with NA % wt. NA Liq. Phase
on 60/80 mesh TENAX-GC Support
Run ISO @ N/A °C using 30 cc/min. He Carrier
@ 75 psig NA Rotameter Rdg. ______
Inlet 160 °C 30°→180° @ 8°/min Type
Detector 160 °C FPD Type (other) NA
Hyd. 40 psig NA Rotameter Rdg. 40 cc/min
Air 70 psig NA Rotameter Rdg. 360 cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 cm/min speed 1 mv F.S. SOLTEC Type
Injection 10 µl indicated 10 µl net 10 µl Actual
Sampling Device GAS SAMPLING VALVE

dimethyl disulfide
ethyl sulfide
methyl sulfide
carbonyl sulfide
sample injection
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
Retention time, minutes

Figure 44. Organic sulfide permeation blend with secondary dilution, concentrated on Tenax-GC trap and thermally desorbed into GC FPD system.

The procedure chosen for the analysis of the organic sulfides consists of (1) collecting the organic sulfides on a Tenax GC trap at -76°C; (2) thermally desorbing the organic sulfides from the trap into the GC sampling system; (3) injecting the organic sulfides into the GC; (4) analysis of the organic sulfides with a GC equipped with a sub-ambient oven accessory, a 6' x 1/8" Teflon analytical column packed with Tenax-GC, and a flame photometric detector; (5) and quantifying the results with the use of permeation calibration tubes. A finalized copy of the procedure is included as an appendix to the interim report.

VALIDATION EXPERIMENTS

Several experiments were carried out to determine the validity of the organic sulfide procedure for the analysis of carbonyl sulfide, methyl sulfide, ethyl sulfide, and methyl disulfide. These experiments included checks for: GC injection variability, linearity of detector response, sample stability in the Tenax traps, trapping efficiency of the Tenax traps, interferences, and test repeatability.

The finalized sampling conditions used to collect the organic sulfides are listed below as is a discussion on their selection. A 2" x 3/8" OD stainless steel trap packed with Tenax-GC is used to collect 99+ percent of the organic sulfides. During sampling, the trap is kept at -76°C in a dry ice-isopropyl alcohol slurry. This temperature is necessary to effectively trap the four organic sulfides from the dilute exhaust sample. Higher temperatures (greater than 0°C) allow carbonyl sulfide to break through the Tenax-GC trap. The other three sulfides can be effectively trapped even at temperatures as high as 20°C. The sample flow rate through the trap is maintained at 130 mℓ/min. At higher flow rates (250 mℓ/min), breakthrough of the organic sulfides occurs. A flip top filter, a Perma Pure Drier, and a trap containing 5 percent sodium bicarbonate on 45/60 mesh Chromosorb P-AW DMCS precede the Tenax GC trap. The flip top filter removes particulate from the gas stream prior to flow through the Perma Pure Drier. If particulate is allowed to enter the Perma Pure Drier, it could poison the drier and prevent it from functioning properly. The Perma Pure Drier removes moisture from the gas stream which could freeze out in the -76°C Tenax-GC trap, thus restricting or stopping flow through the Tenax-GC trap. The 5 percent sodium bicarbonate trap removes sulfur dioxide from the gas stream and prevents it from collecting in the Tenax-GC trap. The sodium bicarbonate trap will remove 10 ppm sulfur dioxide at a sample flow of 130 mℓ/min continuously from dilute exhaust for periods up to 30 minutes. Tenax-GC was chosen as the organic sulfide absorbing material over the other packing materials due to its trapping reproducibility and ability to withstand desorption temperatures.

The Tenax-GC traps can be used many times without replacing the Tenax-GC packing material. There is a large deviation in trapping efficiency from batch to batch of the Tenax-GC packing and each batch must be validated prior to sampling. Each trap is conditioned in an oven operating at 325° ± 25°C for one hour with a flow of zero nitrogen (500 mℓ/min) passing through the trap. No carry over of sulfides in the Tenax-GC traps has been found from test to test. This lack of carry over indicates that the desorption process removes 100 percent of the sulfides collected on the trap.

The sample traps must be stored at -76°C before desorption and analysis or carbonyl sulfide will be lost from the traps. The other three sulfides, methyl sulfide, ethyl sulfide, and methyl disulfide, are stable in the traps overnight at room temperature. In most cases, all traps are run between one half hour and three hours after sampling. The traps are capped after sampling with miniature quick connects to prevent condensation of water and other compounds into the trap before analysis. After the traps have been desorbed, they are again capped to prevent contamination before they are used in sample collection again.

To determine the GC injection repeatability for the organic sulfide procedure, a permeation standard containing 1.95 ppm carbonyl sulfide, 3.31 ppm methyl sulfide, 0.84 ppm ethyl sulfide, and 0.20 ppm methyl disulfide was injected into the GC analytical system six consecutive times. The results of this injection repeatability experiment are presented in Table 43. The percent deviation varies from 1 percent for methyl sulfide to 6 percent for methyl disulfide. This deviation appears to increase with decreasing concentration of organic sulfide.

TABLE 43. INJECTION REPEATABILITY FOR THE ORGANIC SULFIDES

Compound	Average GC Peak Area	Standard Deviation	Percent Deviation
Carbonyl Sulfide	29596	420	1.4
Methyl Sulfide	52325	449	0.9
Ethyl Sulfide	11201	254	2.3
Methyl Disulfide	3951	243	6.2

To determine the test-to-test repeatibility for the procedure two experiments were carried out. In the first experiment, organic sulfides from a diluted permeation blend were collected on a Tenax-GC trap, desorbed into the injection system, and injected into the analytical gas chromatograph system. This sequence was repeated 5 times using the same Tenax-GC trap and the resulting GC peak areas for each of the organic sulfides were averaged over the 5 tests. Standard deviations and percent deviations were also determined for the organic sulfide GC peak areas. The results of this experiment are presented in Table 44. Standard percent deviations ranged from 7 percent for methyl sulfide to 10 percent for carbonyl sulfide and methyl disulfide. The second experiment was identical to the first experiment except that 5 different traps were used to collect the organic sulfides instead of using the same trap 5 times. Table 45 shows the results of this experiment. Standard percent deviations ranged from 13 percent for methyl sulfide to 26 percent for ethyl sulfide.

To determine the linearity of the detector for the concentration ranges of interest, a permeation system containing permeation tubes of all four sulfides was used to generate varying concentrations of the sulfides.

TABLE 44. TRAP REPEATABILITY FOR ORGANIC SULFIDE COLLECTION

	COS Area	Me_2S Area	Et_2S Area	Me_2S_2 Area
Test 1	20241	71938	34417	41346
Test 2	22052	66098	35156	39537
Test 3	20092	74326	38123	41683
Test 4	22343	63777	30508	34147
Test 5	17378	65494	32516	34321
	20421	68327	34144	38207
Standard Deviation	±1985	±4548	±2864	±3718
Percent Deviation	9.7%	6.7%	8.4%	9.7%

TABLE 45. TRAP TO TRAP REPEATABILITY FOR ORGANIC SULFIDE COLLECTION

	COS Area	Me_2S Area	Et_2S Area	Me_2S_2 Area
Test 1	47,590	68,995	25,716	13,839
Test 2	46,830	43,429	20,549	11,487
Test 3	44,465	66,874	17,283	10,069
Test 4	50,590	63,440	30,144	15,901
Test 5	25,788	76,180	16,631	10,338
	43,053	65,784	22,065	12,327
Standard Deviation	±9,896	±8,332	±5,773	±2,491
Percent Deviation	23.0%	12.7%	26.2%	20.2%

Figures 45-48 show plots of the GC peak areas vs. the nanograms of each sulfide injected into the GC system. Carbonyl sulfide and ethyl sulfide give linear responses in the 1-200 ng region, methyl sulfide gives a linear response in the 1-120 ng region, and methyl disulfide gives a linear response in the 1-55 ng (higher levels of methyl disulfide were not tried) region. Above 120 ng of methyl sulfide and 200 ng of carbonyl sulfide, the detector is not linear, with the peak area not increasing proportionally with the weight of sulfide injected. The concentration range of sulfides in dilute exhaust which would fall in this linear range with the current sampling technique is 0.1 to 25 ppb. If the concentration of sulfides in the dilute exhaust exceeds a concentration of 25 ppb, a lower sample flow rate will have to be used in order to collect a smaller amount of the sulfides.

Hydrogen sulfide, sulfur dioxide, thiophene, methyl mercaptan, and ethyl mercaptan are sulfur containing compounds that could interfere with the organic sulfide procedure. Sulfur dioxide is present in exhaust at levels which would obscure all other compounds in the GC procedure if it is not removed before it enters the Tenax-GC trap. A 5 percent sodium bicarbonate trap preceding the Tenax-GC trap effectively removes sulfur dioxide from the exhaust without affecting the concentration of the organic sulfides. Hydrogen sulfide at levels of less than one ppm do not pose a problem with the procedure as no breakthrough of hydrogen sulfide into the Tenax-GC trap is detected by the GC-FPD. However, if hydrogen sulfide is present at concentrations of 4 ppm or greater, some hydrogen sulfide is collected on the Tenax-GC trap and is detected by the GC-FPD. If this higher concentration of hydrogen sulfide is present the GC parameters can be modified to prevent hydrogen sulfide from interfering with the analysis of carbonyl sulfide. An oven temperature program which consists of holding the oven temperature at 0°C for 4 minutes and then programming to 140°C at 8°/minute will separate hydrogen sulfide and carbonyl sulfide by nearly two minutes. This program does extend the analysis time from 25 minutes to 45 minutes if the time it takes to recool the GC oven to 0°C is included. Methyl and ethyl mercaptan have yet to be detected in exhaust. If present, the GC operating conditions will separate these compounds from the sulfides of interest. With the present operating conditions, thiophene has a retention time that differs from ethyl sulfide by only seconds. Thiophene and ethyl sulfide have not been effectively separated by changing the GC operating conditions and therefore, thiophene must be included as a possible source of error in the analysis for ethyl sulfide.

QUALIFICATION EXPERIMENTS

Qualification experiments were carried out using a 1972 Plymouth Fury with a 360 V-8 engine (no catalyst). Hot FTP (23 minute test) driving cycles were followed to generate exhaust for the vehicle baseline emissions and for the tunnel injection plus vehicle experiments. An aluminum cylinder containing 2-5 ppm of each of the organic sulfides in balance nitrogen was used as the source for the organic sulfides. Some tests were conducted with an aluminum cylinder containing 40 ppm carbonyl sulfide in balance nitrogen. The cylinders were named by comparing GC peak areas with the GC peak areas of the organic sulfides generated by the permeation system.

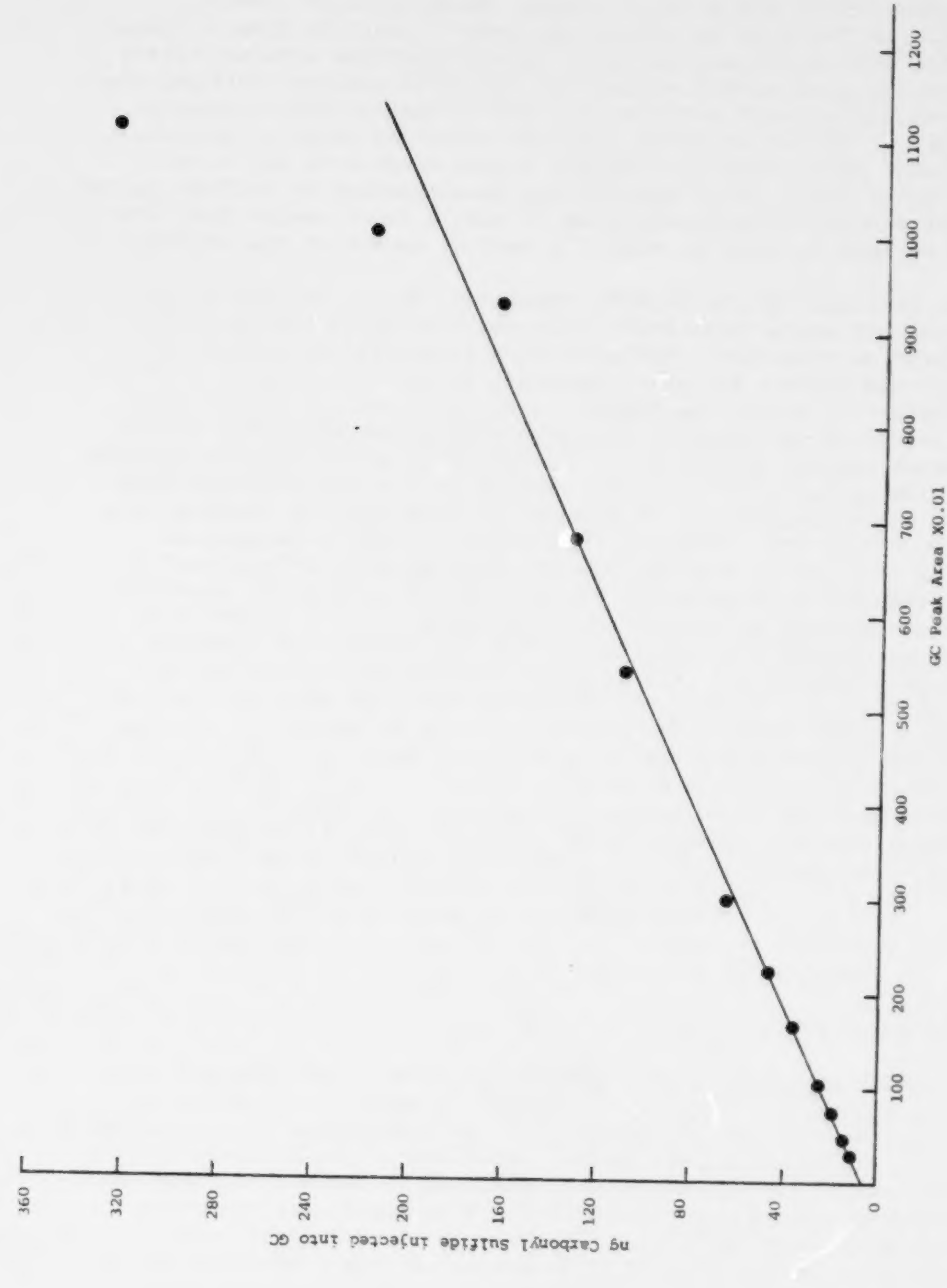


Figure 45. Carbonyl sulfide linearity plot.

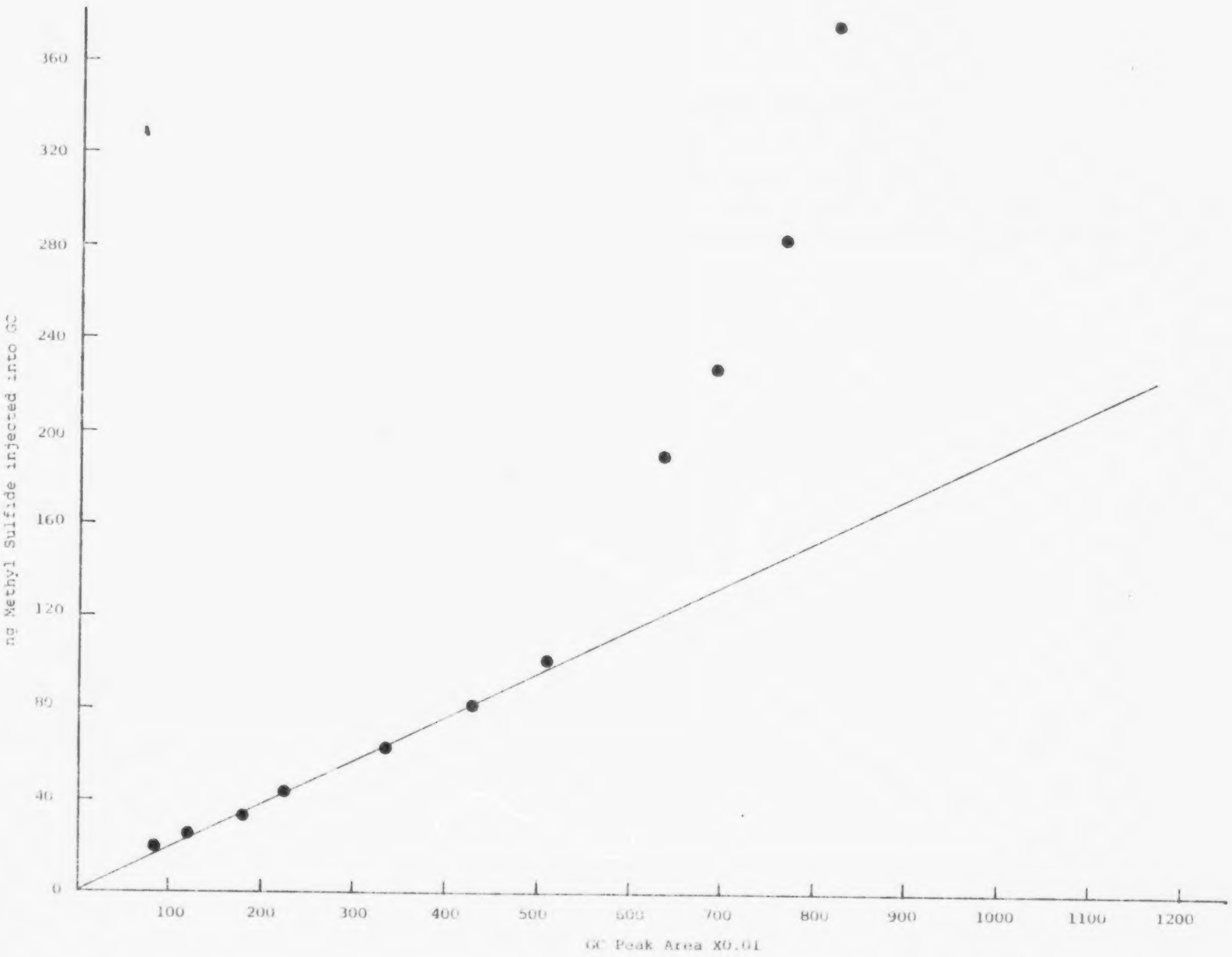


Figure 46. Methyl sulfide linearity plot

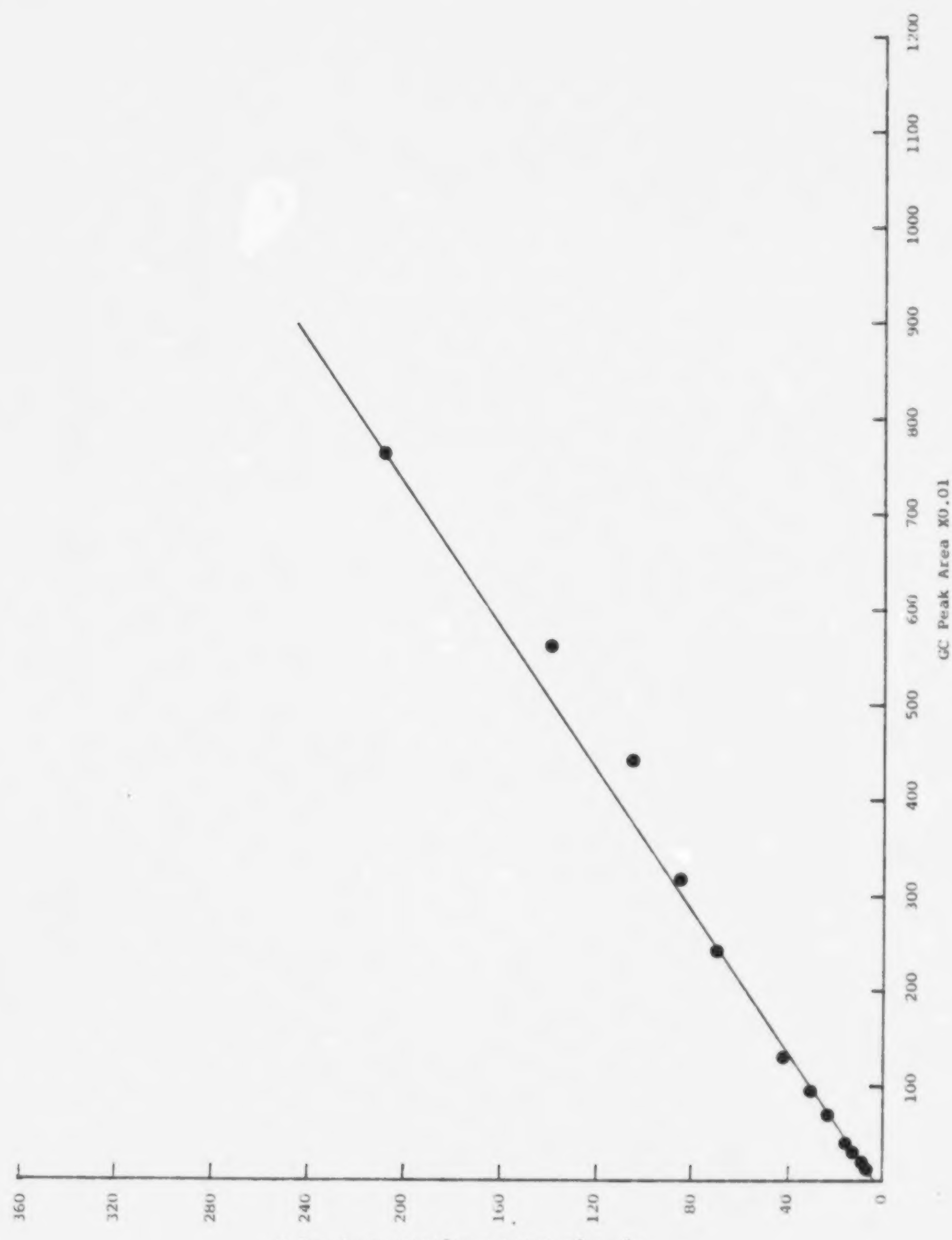


Figure 47. Ethyl sulfide linearity plot.

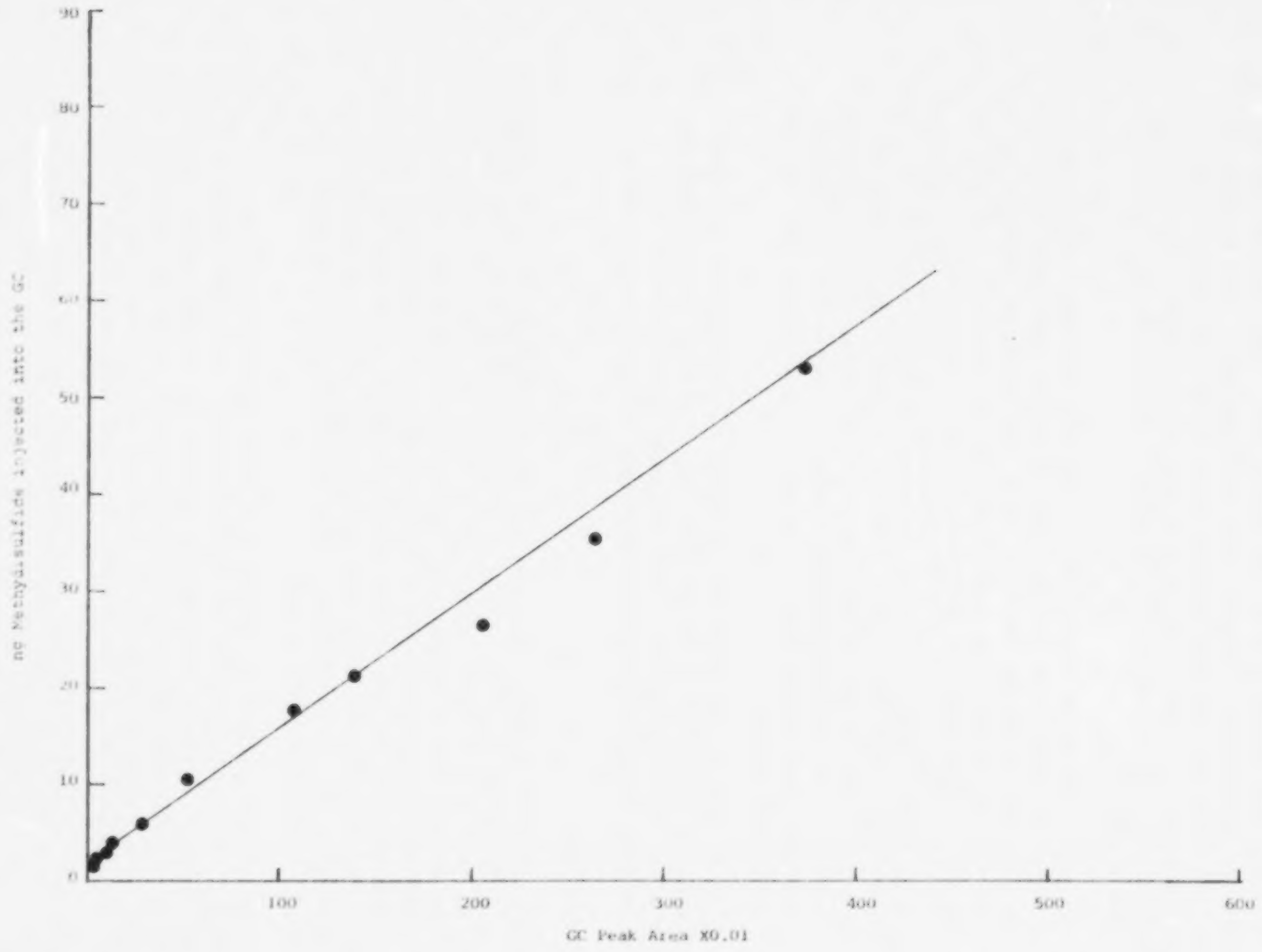


Figure 48. Methyl disulfide linearity plot.

The flow of organic sulfides into the tunnel was regulated to give a concentration of 2-5 ppb of each of the organic sulfides in the dilution tunnel. Injections of the organic sulfides into the tunnel without exhaust gave recoveries that varied from approximately 50 percent for methyl disulfide to 80 percent for carbonyl sulfide (Table 46). The percent deviation of the recovery percentages ranged from 15-20 percent. This value is expected due to the trap-to-trap variations found in the validation experiments. The recovery of the organic sulfides with real exhaust (excluding carbonyl sulfide) varied from 5 percent for methyl disulfide to 20 percent for ethyl sulfide (Table 47).

Carbonyl sulfide recoveries ranged from 0 to 471 percent. The baseline emissions of carbonyl sulfide were erratic and of equal magnitude to the carbonyl sulfide injected into the tunnel. This variation of carbonyl sulfide from the vehicle, along with tunnel memory for carbonyl sulfide, and trap-to-trap variations, made the percent recovery calculations very difficult and thus gave the resulting 0-471 percent recovery. Undocumented recovery experiments with higher concentrations of carbonyl sulfide (0.1 ppm) and vehicle exhaust gave more consistent results, however, the amount of carbonyl sulfide collected on the Tenax trap was out of the linear range of the FPD and values could not be determined. Baseline emissions for methyl sulfide, ethyl sulfide, and methyl disulfide were insignificant and did not affect the recovery experiment.

There is a 20 to 50 percent loss of the organic sulfides in the CVS tunnel without exhaust and a 80 to 90 percent loss (excluding carbonyl sulfide) with exhaust in the CVS tunnel. These losses must be taken into account in determining organic concentrations when using this procedure.

RESULTS AND DISCUSSION

The concentration of organic sulfides can be determined by: 1) trapping the sulfides in a Tenax-GC trap at -76°C, 2) thermally desorbing the sulfides from the Tenax GC trap into the GC injection system, 3) injecting the organic sulfides into the analytical GC system, 4) analyzing the organic sulfides with a gas chromatograph equipped with a flame photometric detector, and 5) quantifying the results by comparison with standards generated by a permeation system. The organic sulfides are effectively caught in the Tenax-GC trap at a flow rate of 130 mℓ/minute. The procedure has a minimum detection limit of approximately 0.2 ppb.

The accuracy of the procedure in the 0.2 to 25 ppb range is on the order of 25 percent due to trap-to-trap repeatability. The FPD gives a linear response for the organic sulfides in the 0.2 to 25 ppb range. If the concentrations of the organic sulfides exceed this range in dilute exhaust, a lower sampling flow rate (less than 130 mℓ/minute) must be used to keep the detector response in the linear range of the detector.

Sulfur dioxide, hydrogen sulfide, and thiophene are possible interferences in the procedure. Sulfur dioxide is removed by the use of a sodium bicarbonate trap, hydrogen sulfide can be separated in the GC system by changing oven parameters; however, thiophene remains an interference to the

TABLE 46. PERCENT RECOVERIES OF THE ORGANIC SULFIDES FROM THE CVS TUNNEL ONLY

	Carbonyl Sulfide (2-40 ppb) Percent Recovery
	87.7
	72.9
	71.8
	107.3
	62.9
	94.1
	79.0
Average % Recovery	82.2%
Standard Deviation	±15.1%

	Methyl Sulfide (5 ppb) Percent Recovery
	69.0
	95.0
	60.2
	56.7
	86.8
Average % Recovery	73.5%
Standard Deviation	±16.7%

	Ethyl Sulfide (2-3 ppb) Percent Recovery
	96.6
	52.1
	50.0
	67.0
	89.8
	68.6
	77.1
	41.7
Average % Recovery	67.9%
Standard Deviation	±19.4%

	Methyl Disulfide (2-4 ppb) Percent Recovery
	84.4
	18.8
	39.0
	48.6
	26.0
	73.8
	53.7
	37.6
	46.4
Average % Recovery	47.6%
Standard Deviation	±21.1%

TABLE 47. PERCENT RECOVERIES OF THE ORGANIC SULFIDES FROM THE CVS TUNNEL AND EXHAUST

	Carbonyl Sulfide (2 ppb) Percent Recovery		Methyl Sulfide (5 ppb) Percent Recovery
	0		3
	0		1
	93		44
	0		13
	120		8
	421		0
Average % Recovery	114%	Average % Recovery	12%
Standard Deviation	±181%	Standard Deviation	±17%

	Ethyl Sulfide (2-3 ppb) Percent Recovery		Methyl Disulfide (4 ppb) Percent Recovery
	25		0
	12		0
	14		0
	16		0
	35		14
	25		8
Average % Recovery	21%	Average % Recovery	4%
Standard Deviation	± 9%	Standrad Deviation	6%

procedure. The ethyl sulfide concentration is affected by this interference. There is a significant loss of the organic sulfides in the CVS tunnel with and without exhaust. These losses must be taken into account in determining the concentrations of the organic sulfides when using this procedure.

Overall, the organic sulfide procedure should provide a relatively accurate method for determining the concentrations of the organic sulfides in dilute exhaust, and its use is recommended for this project.

SECTION 10

NICKEL CARBONYL PROCEDURE

LITERATURE SEARCH

Nickel carbonyl (nickel tetracarbonyl) is a colorless, flammable, highly volatile liquid. It has a melting point of -25°C, a boiling point of 43°C (1 atm), and a density of 1.31 g/mℓ at 20°C. Nickel carbonyl has a musty "damp cellar" or "sooty" odor (110), and can be detected by the human olfactory at 1-3 ppm. In 1968 the American Conference of Governmental Industrial Hygienists recommended a threshold limit of 0.001 ppm for daily exposure without adverse effects. Nickel carbonyl is thermodynamically unstable and decomposes at room temperature.

The toxicity and flammability of nickel carbonyl have provided an impetus for the development of tests to determine low level concentrations. There are several methods available for the detection of nickel carbonyl, including infrared spectroscopy, spark spectroscopy, flame photometry, light reflectance, colorimetry, gas chromatography, and chemiluminescence.

Infrared spectroscopy is reported to have a detection limit of 4 ppm by volume (111). Spark spectroscopy has a 0.1 ppm detection limit, but the exposure time of the photographic plate requires considerable time. The flame photometric method is expensive to operate, requires the use of an open flame, and has a detection limit of 0.1 ppm (112).

There are several colorimetric methods available for the determination of nickel carbonyl. One method traps the nickel carbonyl with a solution of iodine in ethanol or chloroform. The nickel in the absorbing solution is complexed with dimethylglyoxime and measured spectrophotometrically at 400 nm (113,114). The method has a detection limit of 2 ppb, but the collection time is on the order of hours. A second method uses a saturated solution of sulfur in the trifluoroethylene to trap the nickel carbonyl and a UV spectrophotometer to analyze the sample (115). A third method reacts nickel carbonyl with red mercuric oxide at 200°C. This method liberates mercury which is measured spectrographically(116). A fourth method traps the nickel carbonyl in dilute sulfuric acid, and sodium diethyldithiocarbonate is used to complex the nickel. Another method uses chloramine B in ethanol as the absorber, and the nickel is complexed with dimethylgloxime (117). Potassium iodide on silica gel has also been used to collect nickel carbonyl (118). In this method, iodine is released and measured colorimetrically. Still another method uses dilute hydrochloric acid as the absorbing reagent and alphafuridioxime is the complexing agent.

A gas chromatograph with a Carbowax 20 M column and an electron capture detector was employed to determine nickel carbonyl in the blood and breath of rats (119). The technique involved vacuum extraction of nickel carbonyl from the blood and trapping it in cold ethanol (-78°C). The electron capture detector is insensitive to most hydrocarbons but is sensitive to organometallic compounds.

A device has been developed that takes advantage of the thermodynamics of nickel carbonyl (120). In the absence of carbon monoxide, nickel carbonyl decomposes on contact with a hot surface, in this case borosilicate glass. The rate of decomposition is proportional to the nickel carbonyl concentration. The intensity of plane-polarized light reflected from the surface is calibrated in ppm of nickel carbonyl. The detection limit is 0.05 ppm, but this method is also sensitive to iron carbonyl and possibly other metallo-organic gases. Another method which takes advantage of the thermodynamic properties of nickel involves the detection of nickel carbonyl by its pyrolysis products in an ionization chamber (121).

A chemiluminescent measurement which incorporates the light emitting reaction of nickel carbonyl, ozone, and carbon monoxide has been reported to have a detection limit of 0.02 ppb and does not necessitate concentration of the sample (122).

PROCEDURAL DEVELOPMENT

In conjunction with the Project Officer, it was determined that the analysis of nickel carbonyl should be conducted by the use of chemiluminescence. Two instruments are available for the analysis of nickel carbonyl, a modified Teco 12A chemiluminescent analyzer and an EPA supplied chemiluminescent analyzer.

Four aluminum cylinders which were reported to contain 0.1, 1, 5 and 10 ppm of nickel carbonyl in balance carbon monoxide were used as sources of nickel carbonyl in the procedural development experiments.

Since the chemiluminescent detector requires a gaseous sample for analysis, and the chemiluminescent detector has a reported lower detection limit of 0.02 ppb nickel carbonyl, the obvious method for collecting nickel carbonyl for analysis would entail the use of Tedlar sample bags. The system shown in Figure 49 was fabricated to allow for the analysis of nickel carbonyl from bag samples and for the analysis of diluted standard samples obtained from the aluminum cylinders.

The system allows the mixing of small volumes of nickel carbonyl with known large volumes of zero air to obtain ppb levels of nickel carbonyl. The diluted standard (or a bag sample which can be introduced at this point) passes through a 0.5 micron pore size Fluoropore filter to remove any nickel particulate which could interfere with the analysis. The diluted standard or bag sample passes through a pump and is forced under pressure through a needle valve (to regulate flow) and a flowmeter to monitor the flow. At this point, the sample is mixed with an equal volume of carbon monoxide. The presence of carbon monoxide enhances the nickel carbonyl signal and must be

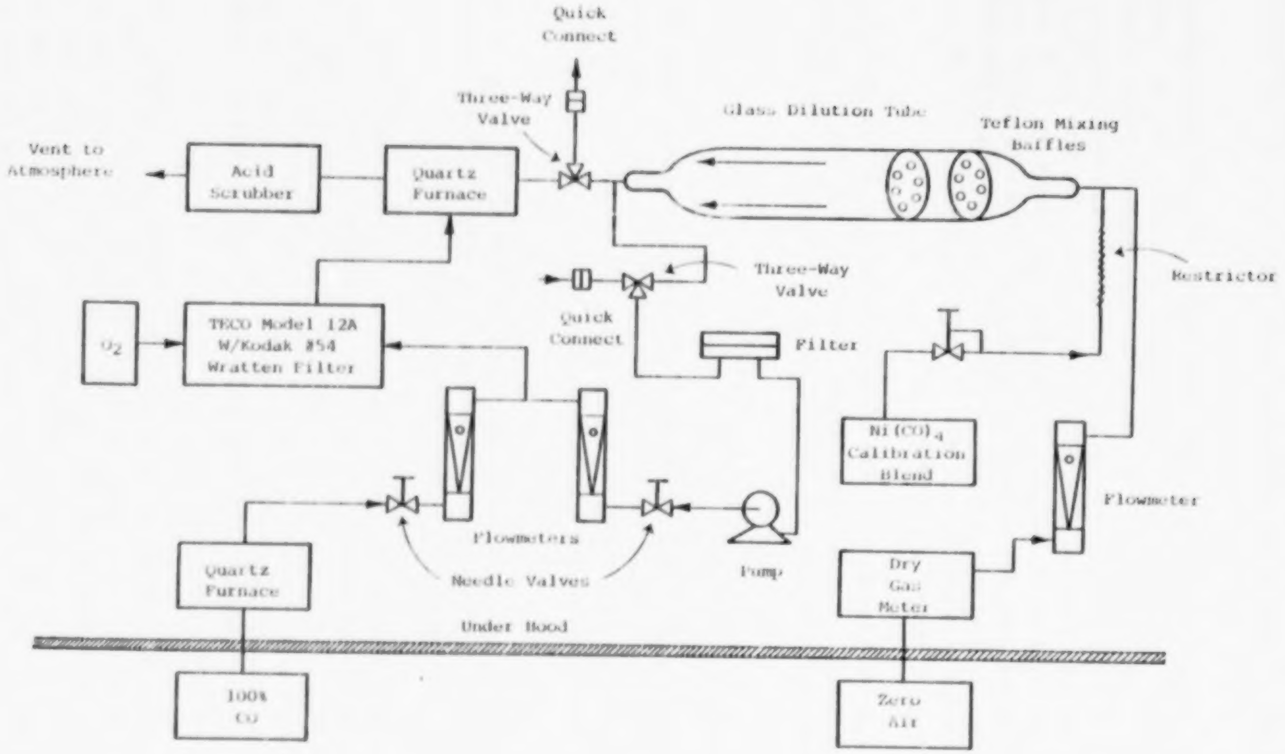

Quick Connect
Three-Way Valve
Glass Dilution Tube
Teflon Mixing Baffles
Vent to Atmosphere
Acid Scrubber
Quartz Furnace
Three-Way Valve
Restrictor
Quick Connect
Filter
O_2
TECO Model 12A W/Kodak #54 Wratten Filter
$Ni(CO)_4$ Calibration Blend
Flowmeter
Flowmeters
Needle Valves
Pump
Quartz Furnace
Dry Gas Meter
Under Hood
100% CO
Zero Air

Figure 49. Nickel carbonyl analysis and dilution system flow schematic.

present for the analysis of sub ppm levels of nickel carbonyl. Before mixing with the sample, the carbon monoxide is passed through a quartz furnace (operating at 480°C) to remove any nickel carbonyl which might be present in the carbon monoxide. The flow rate of carbon monoxide is also regulated with a needle valve and monitored with a flowmeter. The carbon monoxide and sample (bag or diluted standard) mixture enter the chemiluminescent analyzer through the sample line. The sample mixture is split in the analyzer with 95 percent of the mixture exiting the analyzer through the bypass line. This exiting mixture passes through a quartz furnace (480°C) and is bubbled through a nitric acid scrubber to destroy the nickel carbonyl before it is vented to the atmosphere. The remaining 5 percent of the sample-carbon monoxide enters the reaction chamber where nickel carbonyl reacts with ozone (generated by the analyzer) and carbon monoxide to give a light emitting species.

The Teco Model 12A was modified for the detection of nickel carbonyl by replacing the standard CL optical filter with a Kodak No. 74 Wratten filter. The No. 74 Wratten filter allows the light emitted from the nickel carbonyl to enter the detector, but prevents the interfering light of other species from entering the detector. The instrument was evaluated with this filter and found to have interference from nitric oxide and an olefin blend. The No. 74 filter was replaced with a No. 54 Wratten filter to try to remove this interference. This replacement removed the olefin interference and most of the nitric oxide interference. A signal 2-3 times the noise level of the CL instrument still remained for a 80 ppm nitric oxide sample. There is also a fifty fold decrease in the sensitivity of the detector for nickel carbonyl when the No. 74 filter is replaced with the No. 54 filter. The No. 54 filter was selected over the No. 74 filter due to its removal of a large part of the interference signal from nitric oxide. A finalized copy of the nickel carbonyl procedure is included as an appendix to the interim report.

VALIDATION EXPERIMENTS

Several experiments were carried out to determine the validity of the chemiluminescent procedure for the analysis of nickel carbonyl. These experiments included checks for sample stability in Tedlar bags, linearity of detector response, and interfering compounds.

Nickel carbonyl in balance carbon monoxide has a half life of several weeks in Tedlar bags. In the presence of ambient air or exhaust, ppb levels of nickel carbonyl are unstable and have half lives on the order of 40-70 minutes. The half life of nickel carbonyl in air or exhaust increases with increasing concentration of carbon monoxide in the Tedlar bags. The use of dark or clear bags has little or no effect on the stability of the nickel carbonyl.

To determine the linearity of the chemiluminescent detector, nickel carbonyl in balance carbon monoxide was diluted with zero air to give varying concentrations of nickel carbonyl. Figures 50 and 51 show dilution ratios vs peak height for the instrument with the No. 54 and No. 74 Wratten filters. The chemiluminescent detector (with either the No. 54 or the No. 74 filter) gives a linear response for nickel carbonyl down to the detection limits of the instrument.

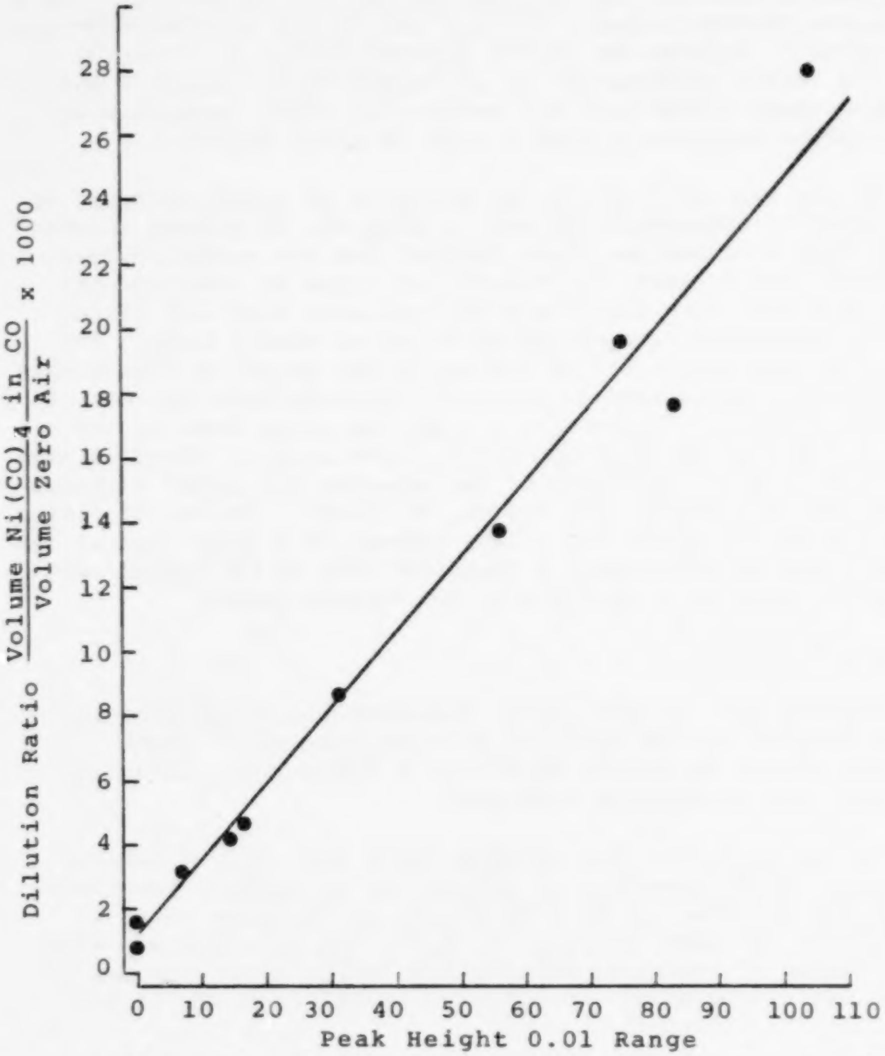


Figure 50. CL detector linearity for nickel carbonyl with a No. 74 Wratten filter.

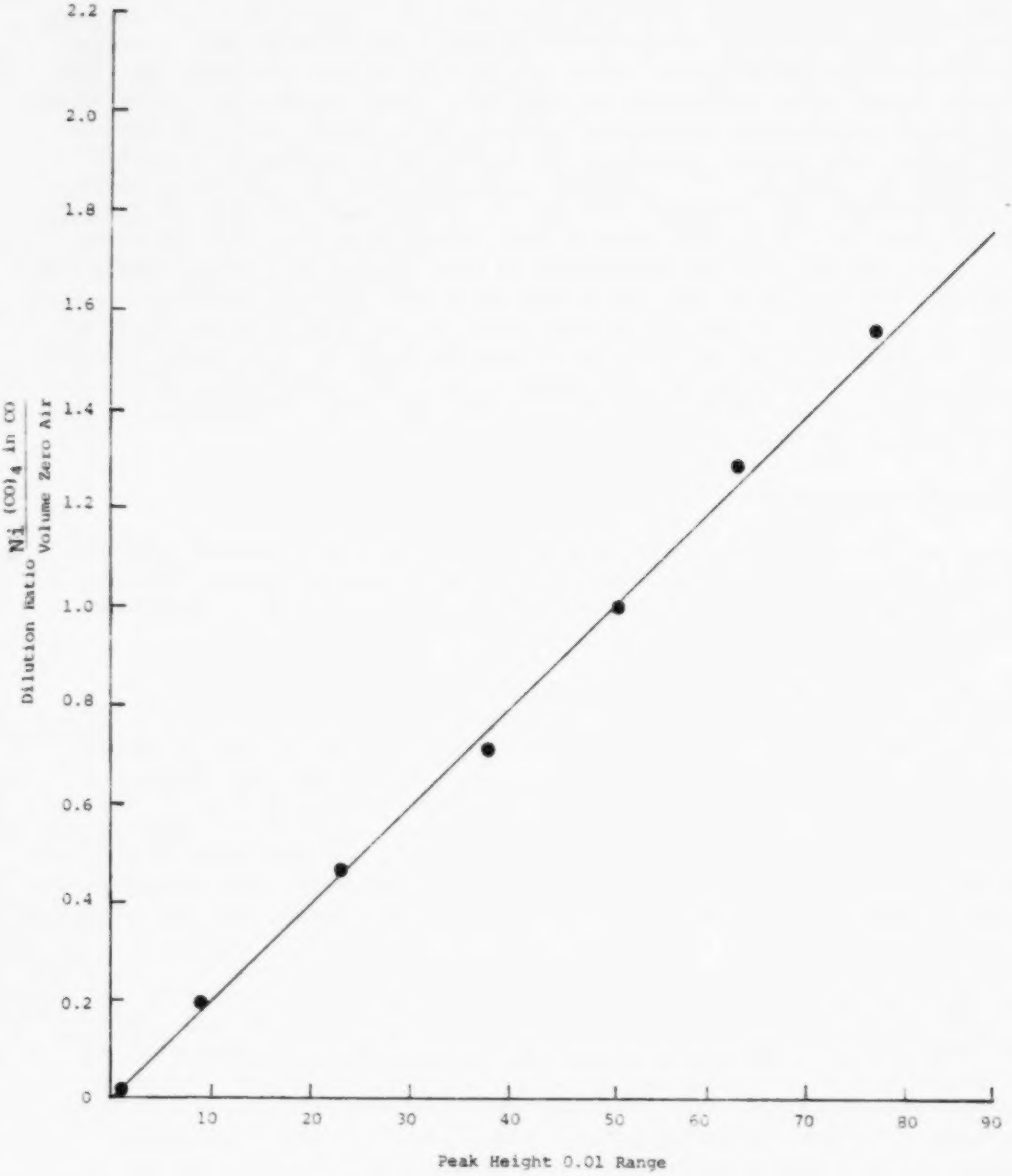


Figure 51. CL linearity for nickel carbonyl with No. 54 Wratten filter.

Interference checks were carried out on the chemiluminescent detector with the No. 74 filter and the No. 54 filter installed. Olefins and nitric oxide give interfering signals when the No. 74 filter is installed. A hydrocarbon blend containing 13.7 ppm ethylene, 20.7 ppm propylene, as well as methane, ethane, propane, acetylene, benzene, and toluene gave a signal equivalent to 0.002 ppb $Ni(CO)_4$. When the No. 54 filter is installed, the interfering signal from this blend is removed. When the No. 74 filter is in use, the major interfering species is nitric oxide, which has a rejection ratio of 0.002. The signal generated by nitric oxide compared to nickel carbonyl will be large and its presence would make the analysis for nickel carbonyl difficult. By replacing the No. 74 filter with the No. 54 filter, most of the interfering nitric oxide signal was removed. A 3000 fold decrease in the response of the instrument to a 80 ppm nitric oxide sample was observed when the No. 54 filter was substituted for the No. 74 filter. The remaining nitric oxide signal is on the order of 2-3 times the noise level of the CL instrument. However, a fifty fold decrease in the sensitivity of the instrument to nickel carbonyl is experienced when the No. 54 filter is substituted for the No. 74 filter. Even with this loss of sensitivity, the detection limits are less than 0.1 ppb.

QUALIFICATION EXPERIMENTS

Based on the desires of the Project Officer, no CVS recovery experiments were attempted with nickel carbonyl. The potential health hazards of nickel carbonyl injections into the CVS were not considered justified under these circumstances.

RESULTS AND DISCUSSION

The concentration of nickel carbonyl in dilute exhaust can be determined by collecting the exhaust samples in Tedlar bags and analyzing the samples with a chemiluminescent detector which has been modified by the use of a No. 54 Wratten filter. The procedure has a detection limit on the order of 0.1 ppb. The exact determination of the lower detection limit, as well as the quantification of the results of the analysis, are difficult as the nickel carbonyl standards have been found to be unstable and give varying results.

The exhaust bag samples must be analyzed as quickly as possible as nickel carbonyl is unstable in exhaust and has a half life on the order of 40-70 minutes. Nitric oxide is an interference in the procedure with an 80 ppm concentration of nitric oxide giving a response of about twice to three times the noise level of the instrument. The levels of nitric oxide must be monitored when interpreting any response from this instrument. This procedure will allow the detection of nickel carbonyl in exhaust at sub ppm levels if proper documentation and precautions are undertaken when interpreting any results using this method of detection.

SECTION 11

AMMONIA PROCEDURE

LITERATURE SEARCH

Ammonia is a colorless, corrosive, and weakly alkaline gas with a distinctive pungent odor. It has a molecular weight of 17.03, a boiling point of -33.35°C (1 atm), and a freezing point of -77.7°C (1 atm). The ammonia molecule is pyramidal in shape with N-H and H-H bond distances of 1.016 and 1.645 Å, respectively. The H-N-H bond angle is 106.67°. Ammonia is soluble in water, ethanol, methanol, chloroform, and ether. The basic nature of ammonia allows it to react with protonic acids to form water soluble ammonium salts. It also reacts to form stable metallic complexes. Chemically, ammonia is a highly associated, stable gas with only slight dissociation at 840-930°C and atmospheric pressure. The toxicity level of ammonia for humans is about 1700 ppm with an exposure of less than 30 minutes; however, the 1968 American Conference of Governmental Industrial Hygienists recommended a threshold limit of 50 ppm, the amount to which most workers may be exposed to repeatedly day after day without adverse affects. Ammonia poisoning is not necessarily a serious health hazard though its odor is perceptible at 20-50 ppm (5, 123, 124). Commercially, ammonia is produced by the Haber Process according to the reaction:

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$$

The reaction is carried out at 400-450°C and 200-600 atm over a specially prepared catalyst composed of iron, potassium oxide, and aluminum oxide. The most extensive use of ammonia in industry is in soil fertilization. It is also widely used to manufacture nitric acid via the Ostwald process (5, 124).

A number of methods for ammonia analysis are available; however, most of these methods are subject to interferences, especially from volatile amines. These interferences affect a number of colorimetric procedures. Nessler's reagent is sensitive to formaldehyde, alcohols, organic compounds, amines, sulfides, acetone, and aldehydes (125). Distillation is necessary to remove these interferences. The indophenol method is more sensitive than Nessler's (126), but it too suffers from contamination by formaldehyde, SO_2 (10:1), Fe, Cr, Mn, and Cu (127). During color development pH must be carefully controlled for reliable results (126). Another highly sensitive procedure is the pyridine-pyrazalone method. It is very involved and is susceptible to interference from some cations at high concentrations (128). A direct colorimetric method for ammonia analysis involves collection in a neutral solvent (dioxane) containing a quinone and subsequent absorbance measurement at 480 nm on a spectrophotometer. The major drawback of this procedure is that one of the reagents, o-(benzenesulfonamide)-p-benzoquinone, must be synthesized, purified, extracted with benzene, and recrystalized before use (129). As with the colorimetric methods, the most serious weakness of titrimetry methods is the large number of interferences. The Kjeldahl procedure includes a distillation step, but this does not eliminate the interference from volatile amines because they, too, distill over. The classical titrimetry methods, acidimetry, complexometry, oxidimetry, and formal titration are also used for the determination of ammonia, but they are generally limited to 10^{-4} M solutions. Several instrumental optical methods are used in ammonia analysis. These include the chloramine (130), cupriammonia complex (131), ninhydrin (132), and electroanalytical methods. Additionally, there is a method for direct measurement on a spectrophotometer with a UV (133, 134) or IR (135, 136) detector as well as a number of indirect colorimetric methods (137). Gas (138, 139) and paper (140) chromatography have been employed successfully for some applications. A number of electrochemical techniques have also been developed for ammonia analysis. Among these are amperometry, polarography, and coulometric acidimetry, and oxidation (141,142). Interferences again pose a problem with these procedures. The specific ion electrode for ammonia is a relatively rapid and direct electrochemical method for determination of ammonia. However, since a longer equilibration time (about 20 minutes) is required for low NH_3 concentrations, the ammonia gas tends to escape from the basic solution. This long equilibration time causes unreliable results in the concentration range of interest (143). Volatile amines interfere with analysis (144), and the hydrophobic membrane of the electrode has been found to deteriorate in 2 to 3 weeks (143).

Both gasometric (145-147) and gravemetric (146,148, 149, 150) techniques are not sensitive enough for trace analysis, and the chemiluminescent procedure is more involved than is practical (151,152). The disadvantage of an enzymatic method reacting ammonia, an α-keto ester, and reduced nicotinamide adenine dinucleotide (NADH) is the high cost of NADH (129).

Ammonia has been quantitatively measured in dilute automotive exhaust using an ion chromatograph. This procedure is free from many of the common interferences that plague the classical methods. The short analysis time (10-15 minutes) makes it a prime candidate for ammonia measurement.

PROCEDURAL DEVELOPMENT

The procedure chosen for the analysis of ammonia involves the use of a new type of liquid chromatograph called an ion chromatograph. Ion chromatographic analysis is direct, relatively rapid (15-20 minutes), and sensitive to 0.01 ppm NH_3. Heavy metals will contaminate the system, and sodium and potassium ions interfere with ammonia detection at 2 ppm and 0.5 ppm, respectively. However, the most common and troublesome interferences, volatile amines, do not affact ammonia analysis on the ion chromatograph. The standards made up in water and the samples collected in a weak acid solution remain stable for at least a month allowing some delay time before processing. These advantages made the ion chromatograph the best choice as a means of measuring ammonia.

Very little procedural development was necessary for this method of analysis. Basically, instrument and sampling parameters needed to be chosen. Suggested instrument variables such as type and strength of eluent, flowrate, chartspeed, and separator column size were provided with the ion chromatograph. These will change somewhat with each set of columns. Ultra pure nitric acid and distilled water have been found to give the best baseline and most rapid recovery from suppressor column regeneration. The regenerant solution is a 0.5N NaOH solution made from reagent grade sodium hydroxide. Chartspeed was set at 12 in/hour, and the flowrate at about 40 percent of fullscale. Good separation was obtained with a 6 × 250 mm separator column. A 3 × 150 mm precolumn (packed with the same resin as the separator column) was placed on line prior to the separator column to trap heavy metals and particulate. If these contaminates get past the precolumn they will poison the separator and suppressor columns. The precolumn can be cleaned weekly with a strong acid solution, as can the separator column if resolution deteriorates.

The sampling parameters were determined as part of the validation experiments. A sampling rate of 2 lit/min at ice bath temperatures was found to be most efficient. Two bubblers containing 25 mℓ of 0.01 N H_2SO_4 capture over 99 percent of the ammonia passing through. A 0.5 micron fluoropore filter was inserted on line before the bubbler to trap exhaust particulate. It is necessary to heat the line from 150 to 170°F to prevent moisture condensation and thus ammonia capture in the sample line.

VALIDATION EXPERIMENTS

The first validation experiment conducted involved the selction of sampling parameters: flowrate, collection temperature, number of bubblers, absorbing reagent, filter and the use of heated or unheated sampling lines. The most efficient flowrate and temperature combination was determined to be 2 ℓ/min at ice bath temperature. The data from these collection efficiency tests if found in Table 48. Ninety-five percent of the ammonia was collected at these conditions compared with 84 percent at 4 ℓ/min, ice bath, 90 percent at 2 ℓ/min, room temperature, and 92 percent at 4 ℓ/min, room temperature. Table 48 shows that 98.4 percent of total ammonia was trapped in the first bubbler and 99.1 percent in the first two bubblers when the nominal 100 ppm NH_3 flow was diluted 1:5. With the 1:20 flow dilution 99.3 percent of the ammonia remained in bubbler one and 99.6 percent in bubblers one and two. Two tapered tip bubblers containing 25 mℓ of 0.01N H_2SO_4 as the absorbing solution are therefore used to trap 99+ percent of the NH_3. Increasing the acidity of the absorbant (0.06N) causes interference with the ion chromatographic analysis by broadening the eluted peaks. Of significant importance is column contamination that occurs if particulate is not filtered from the sample prior to analysis. To prevent this contamination fluoropore filters and heated sample lines are used. The heated lines prevent condensation of water and the loss of ammonia in the sample line. A test was conducted to determine if the filter retained any ammonia. A 1978 Oldsmobile Cutlass was run on the FTP cold driving cycle. 0.12 ppm NH_3 was recovered from the filtered sample line and 0.11 ppm NH_3 from the unfiltered sample line, a difference of 0.01 ppm ammonia. A second test was performed during the recovery of ammonia experiment after injection of 1 percent NH_3 into the exhaust

TABLE 48. NH_3 COLLECTION EFFICIENCY AS A FUNCTION OF FLOWRATE AND TEMPERATURE

Test	Flowrate(ℓ/min)	Temperature(°F)		NH_3 concentration (ppm) and (percent) in bubbler			Bubbler 1+2+3 (ppm)	NH_3 concentration corrected for flow dilution
				1	2	3		
				Ammonia flow diluted 1:5 with zero nitrogen				
1	2	32		17.10(99.6)	0.06(0.4)	0	17.16	85.80
2	2	32		19.51(99.5)	0.10(0.5)	0	19.61	98.08
3	2	32		18.34(95.2)	0.28(1.5)	0.64(3.3)	19.27	96.33
4	2	32		19.59(99.5)	0.06(0.3)	0.08(0.2)	19.68	98.40
			Average	18.64(98.4)	0.13(0.7)	0.17(0.9)	18.93	94.60
5	4	32		16.24(99.4	0.02(0.1)	0.07(0.4)	16.33	81.66
6	4	32		17.40(100)	0	0	17.40	87.00
7	4	32		14.17(98.3)	0	0.24(1.7)	14.41	72.06
8	4	32		17.89(99.0)	0.11(0.6)	0.07(0.4)	18.06	90.33
9	4	32		17.79(99.9)	0.02(0.1)	0	17.81	89.03
			Average	16.70(99.3)	0.03(0.2)	0.08(0.5)	16.80	84.02
10	2	74		17.84(100)	0	0	17.84	89.21
11	2	74		17.87(98.5)	0.17(1.0)	0.10(0.5)	18.14	90.70
			Average	17.86(99.2)	0.09(0.5)	0.05(0.3)	17.99	89.96
12	4	75		18.83(99.4)	0.02(0.1)	0.10(0.6)	18.94	94.72
13	4	74		18.05(100)	0	0	18.05	90.25
			Average	18.44(99.7)	0.01(0.05)	0.05(0.3)	18.50	92.48
				Ammonia flow diluted 1:20 with zero nitrogen				
14	2	32		4.32(99.7)	0	0.01(0.3)	4.33	86.63
15	2	32		4.15(98.9)	0.02(0.5)	0.03(0.6)	4.20	84.00
			Average	4.24(99.3)	0.01(0.3)	0.02(0.4)	4.27	85.32

of the 1972 Plymouth test car. In the first run a loss of 29 percent NH_3 (0.93 ppm) was noted in the filter in comparison to the unfiltered sample and a loss of 55 percent (2.38 ppm NH_3) in the filtered sample was observed in the second run. Due to the great ammonia loss to the filter, fluoropore filters are not used in the ammonia sampling line. Another test was conducted with heated and unheated sample lines to determine the effect on the amount of ammonia recovered. Two injections of 0.1 percent NH_3 were made into the CVS (constant volume sampler) for 25 minutes each. Two of the sample lines were heated and one was unheated. The first of the heated lines had a filter. The third test allowed a 10 minute soak and then the CVS was run for 25 minutes by itself. After the third test the CVS was allowed to run for 30 minutes before sampling for 25 minutes in the fourth test. The CVS was allowed to run for 1 hour and 10 minutes before the fifth test. The sampling period was again 25 minutes. The results of these tests are shown in Table 49. After the ammonia injections, it is obvious that a problem is noted with the unheated lines. The amount of ammonia captured in the second test is double the amount caught in the first. The ammonia values in test 3 - 5 also remain higher than those obatined with heated sample lines. It appears that some ammonia sticks to the unheated sample lines and is never completely removed. For these reasons heated sample lines were used. The column can be poisoned by heavy metals present in the exhaust. These compounds adhere to the column resin and will slowly elute causing broad, unidentifiable peaks to appear periodically. To prevent contamination, a strong nitric acid solution (1 N HNO_3) is used to wash the precolumn weekly. If the separtor column becomes contaminated it is washed similarly. The lighter metals such as sodium and potassium elute within a reasonable length of time (less than 12 minutes), but they can interfere with the ammonia peak beacuse their retention times are close to that of ammonia. Sodium, present in the water supply, interferes when its concentration exceed 2 µg Na^+/mℓ. The tolerable limit for potassium is only 0.5 µg K^+/mℓ. Its presence is due to the incomplete rinsing of glassware washed in chromic acid solution. The absorbing solution, 0.01N H_2SO_4, produces a small peak with the same retention time as ammonia, but a correction is made for this by taking a background sample each testing day. Filtered deionized water interferes negligibly (<0.01 ppm) with ammonia analysis.

Another variable for which validation tests were run is the ion chromatograph. The proper combination of eluent, columns, flowrate, and sample loop size are reuired to obtain optimum results. 0.0075N HNO_3 flowing at 200 mℓ/hour allows good separation between peaks when a 3 × 150 mm precolumn, a 6 × 250 mm separator column, and a 9 × 250 mm suppressor column are used. These parameters will vary between column sets, making it necessary to check the eluent and flowrate when columns are changed. A small loop (0.01 mℓ or 0.2 mℓ) prevents the relatively small ammonia signal from being overwhelmed by the large hydrogen ion peak. An attempt was made to neutralize the acid collection medium with sodium and potassium hydroxide, but the sodium and potassium interferences were too large to make it practical. Injection repeatability figures are shown in Table 50. The mean or average for each set of peak heights and areas is represented by $\bar{x}$, the standard deviation by s_x, and the coefficient of variation in percent by Cv. The coefficient of variation serves as a comparison between injections made on the two days. This value is simply the standard deviation divided by the mean and multiplied by 100. Calculations are done using peak areas rather than peak

TABLE 49. RETENTION OF AMMONIA IN CVS (constant volume sampler)

	Sample Line			
	$1^{a,b}$	2^{b}	averages of 1 and 2	3^{c}
1^{d}	0.60 ppm	0.77 ppm	0.68 ppm	0.62 ppm
2^{d}	0.71	0.55	0.63	1.35
3^{e}	0.06	0.14	0.10	0.41
4^{e}	0.05	0.03	0.04	0.15
5^{e}	0.05	0.05	0.05	0.18

[a] 0.5 micron Fluoropore filter inserted in sample line prior to bubblers.
[b] Heated sample lines.
[c] Unheated sample lines.
[d] 0.1 percent NH_3 injected into CVS.
[e] CVS run with no NH_3 injected.

TABLE 50. INJECTION REPEATABILITY FOR ION CHROMATOGRAPH

Sample	Date	Concentration $(\frac{\mu g\ NH_4^+}{m\ell})$	Attenuation (μmho)		Height (in)	Area
1	3-29-78	0.50	3		0.53	30990
2	3-29-78	0.50	3		0.54	30374
3	3-29-78	0.50	3		0.53	29891
4	3-29-78	0.50	3		0.53	29665
5	3-29-78	0.50	3		0.50	28947
				$\bar{x}$	0.53	29973
				s_x	0.01	766
				Cv	2.8%	2.6%
1	5-09-78	0.50	3		0.51	24335
2	5-09-78	0.50	3		0.51	23205
3	5-09-78	0.50	3		0.51	24785
				$\bar{x}$	0.51	24108
				s_x	0.00	814
				Cv	0.0	3.4%

heights because on the whole they were more reliable. (Peak heights tended to vary with width even though the area counts remained the same). The average variation in areas on the two days ran about 3.0 percent. A comparison was also made on the repeatability of standard preparation. Four 0.5 $\frac{\mu g\ NH_4^+}{m\ell}$ standards were made up using the same stock solution and analyzed on the ion chromatograph. The results are shown in Table 51.

TABLE 51. REPEATABILITY OF AMMONIA STANDARD PREPARATION

Sample	Concentration($\frac{\mu g\ NH_4^+}{m\ell}$)	Attenuation	Height(in)	Area
1	0.50	3	0.50	28947
2	0.50	3	0.53	29821
3	0.50	3	0.52	29011
4	0.50	3	0.50	26819
			$\bar{x}$ 0.50	28650
			s_x 0.015	1284
			Cv 2.9%	4.5%

The coefficient of variation for the area is 4.5 percent. Subtracting the Cv for injection repeatability, the repeatability of standard preparation turns out to be 1.5 percent. A 4.5 percent error then is to be expected from the instrument and standards. The particular combination of columns and the condition of the suppressor column determines the actual repeatability.

The ion chromatograph gives linear response to ammonia at the sensitivity settings of 3 µmho and 10 µmho. Table 52 lists concentrations and corresponding heights and areas of points on the calibration curve. These values are plotted graphically in Figure 52. $(NH_4)_2SO_4$ standards ranging from about 0.4 to 30 $\frac{\mu g\ NH_4^+}{m\ell}$ (ppm NH_4^+) were run at the appropriate attenuations, 3 or 10 µgmo. The areas recorded at 10 µmho were corrected to 3 µmho by multiplying by 10/3. Both scales show linearity but the slopes are visually different with relative values of 1.6 and 1.2 for the and the 10 µmho scales, respectively. The 3 µmho scale remains linear from at least 0.4 to 8 µg NH_4^+/mℓ and the 10 µmho scale from 8 to 30 µg NH_4^+/mℓ.

Sample and standard stability as a function of time was another factor investigated. The sample was a background sample taken during the three bag FTP, SET-7, and FET driving cycles on May 29, 1978, and standard used for comparison (0.5 $\frac{\mu g\ NH_4^+}{m\ell}$) was prepared on May 29, 1978. The same test car

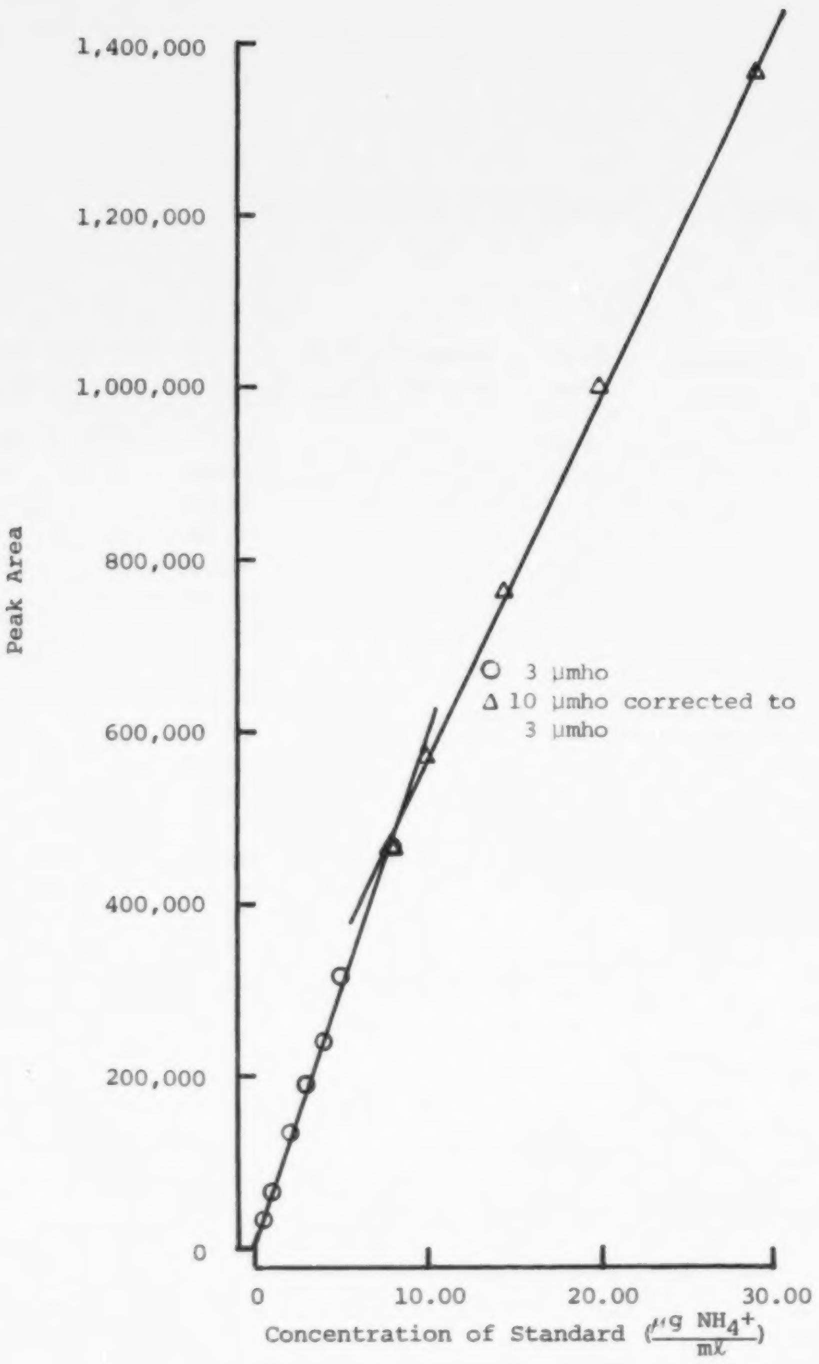


Figure 52. Ammonia calibration curve

TABLE 52. CALIBRATION CURVE FOR AMMONIA

Standard Concentration ($\frac{\mu g\ NH_4^+}{m\ell}$)	Attenuation (μmho)	Height (in)	Heights corrected to 3 μmho scale	Area	Area corrected to 3 μmho scale
0.36	3	0.38		20,987	
0.50	3	0.56		33,412	
0.72	3	0.79		43,798	
1.00	3	1.17		65,530	
1.44	3	1.68		94,950	
1.50	3	1.89		101,103	
2.00	3	2.41		133,785	
3.00	3	3.57		188,785	
3.61	3	4.21		225,901	
4.00	3	4.56		238,585	
5.00	3	5.52		315,582	
7.22	3	7.50		423,980	
8.00	3	8.49		473,131	
8.00	10	2.49	8.30	141,874	472,913
10.00	10	2.93	9.77	170,430	568,100
14.43	10	3.97	13.23	228,363	761,210
20.00	10	4.78	15.93	299,706	999,020
28.86	10	6.30	21.00	409,068	1,363,560

used in previous test procedures was used for this particular test. It is obvious from the data presented in Table 53 that the sample and standard are stable for at least three weeks (23 days). The drop to zero ammonia and the jump to 0.02 ppm NH_3 on the thirtieth and thirty-second days, respectively, are probably due to instrument variation rather than sample degeneration. By the fortieth day (sixth week), however, the increase in ammonia concentrations is by 0.02 ppm. At this point the sample has probably begun to lose integrity. This is further confirmed by the fact that a ten week old FTP sample increased from 0.47 to 0.55 ppm NH_3 (17.0 percent) and that two thirteen week old FTP and FET samples increased from 0.08 to 0.11 ppm NH_3 (37.5 percent) and from 0.17 to 0.23 ppm NH_3 (35.3 percent). It appears that after six weeks the sample concentration begins to increase sharply, indicating a sample and standard lifetime of four to five weeks.

TABLE 53. SAMPLE AND STANDARD STABILITY AS A FUNCTION OF TIME

Date of Analysis	Age of Sample(days)	Concentration(ppm NH_3)
5-29	1	0.01
5-30	2	0.01
5-31	3	0.01
6-01	4	0.01
6-02	5	0.01
6-05	8	0.01
6-13	16	0.01
6-20	23	0.01
6-27	30	0.00
6-29	32	0.02
7-07	40	0.03

QUALIFICATION EXPERIMENTS

The qualification tests for the ammonia procedure included determining a baseline ammonia emission level produced by the test car and determining ammonia recoveries from injection of nominal 0.1 percent NH_3 and 1.0 percent NH_3 into the exhaust of the test car and into the constant volume sampler (CVS) alone. The test car for these experiments was a noncatalyst 1972 Plymouth Fury equipped with a 360 V8 engine. The baseline ammonia emission level for this car ran about 0.07 ppm as shown in Table 54. An injection

TABLE 54. AMMONIA BASELINE FROM PLYMOUTH FURY CAR

Test	NH_3 Concentration(ppm NH_3)
1	0.07
2	0.09
3	0.11
AVERAGE	0.07 ppm NH_3

of 0.1 percent NH_3 was made into the CVS to determine the amount of ammonia that is lost in the CVS tunnel (Table 55). A similar injection was made into the exhaust of the Plymouth Fury during the hot FTP driving cycle. 64.9 percent of the ammonia was recovered from the CVS injection, however, as the data in Table 56 indicates, no constant recovery figure was obtained for the injection of 0.1 percent ammonia into the exhaust of the test car. With seccessive injections the recovery of ammonia increase, from 2 percent to 31 percent. This trend was confirmed by subsequent injections of 1 percent NH_3 into the exhaust of the same test car. These values are shown in Table 57. Although the recoveries are larger due to the higher concentration of ammonia injected, it is obvious that the recovery of ammonia increases with each successive test (from 41 percent to 62 percent). An additional test was conducted to determine ammonia retention in the CVS. The experiment is described in the validation section of this report, and the results are found in Table 49. The obvious differences in ammonia recovery due to heated or unheated sample line are noted in the validation section. However, for both types of sample lines, the length of time the CVS must run beofre a constant level of ammonia is obtained is about the same. After the last injection of ammonia, test 2, and by the end of test 3 (25-minutes with the CVS on), an 84 percent and a 70 percent drop occurs in ammonia recovered after passing through heated an unheated lines, repsectively. By the end of test 3 (80 minutes with CVS on) a 62 percent drop in ammonia level occurs from the sample emerging from the heated line and a 64 percent drop in the sample concentration from the unheated line. Thereafter, the fluctuation appears to be due to random error since the concentration of ammonia increases slightly: 0.04 to 0.05 ppm with heated lines and 0.15 to 0.18 ppm NH_3 with unheated lines. A CVS "wash out" period of an hour to an hour and a half is required to remove between 85 percent and 94 percent of the NH_3 trapped in the CVS after ammonia injection. Following this leveling off, no further decrease in ammonia concentration occurs with additional running of the CVS.

RESULTS AND DISCUSSION

The ion chromatograph was chosen as the most favorable means of measuring ammonia becuase of the simple, direct, and rapid processing of samples. Most compounds that interfere with alternate ammonia procedures do not affect ammonia analysis on the ion chromatograph. The selectivity and sensitivity of this method warrants its use for the analysis of dilute auto-

TABLE 55. AMMONIA RECOVERY FROM DIRECT CVS INJECTION

Test	Nominal Flow Rate (ft^3/min)		Ammonia Injected		Ammonia Recovered			
	NH_3	CVS	[a]volume NH_3 injected (ft^3)	Concentration NH_3 injected (ppm)	[a]Total diulted volume (ft^3)	Sample Concentration (ppm)	Calculated Amount of NH_3 recovered (ppm)	Percent Recovery
1	0.36	315	8.416	908	7907	0.66	0.97	68.3
2	0.36	315	8.485	908	7913	0.63	0.97	64.7
3	0.42	315	9.947	908	7859	0.71	1.15	61.8
								AVG.= 64.9%

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[a] Volume corrected to 1atm and 68°F

[b] This concentration representing 100 percent recovery, was obtained by backcalculating from recovered sample concentration and percent recovery.

TABLE 56. AMMONIA RECOVERY FROM DILUTE EXHAUST BY DIRECT CVS INJECTION OF 0.1 PERCENT NH_3 DURING THE HOT FTP DRIVING CYCLE

Test	Nominal Flow Rate (ft^3/min)		NH_3 Injected		NH_3 Recovered		Calculated amount of NH_3 recovered (ppm)[a]	Percent Recovery
	NH_3	CVS	Volume NH_3 injected (ft^3)[b]	Concentration NH_3 injected (ppm)	Total Diluted Volume (ft^3)[b]	Sample Concentration (ppm NH_3)[c]		
1	0.39	315	8.545	908	7230	0.02	1.07	1.9
2	0.40	314	8.471	908	7188	0.19	1.07	17.8
3	0.39	315	8.376	908	7218	0.33	1.05	31.3

[a] This concentration, representing 100 percent recovery, was o-tained by back calculating from recovered sample concentration and percent recovery.

[b] Volume corrected to 1atm pressure and 68°F.

[c] Includes baseline correction

TABLE 57. AMMONIA RECOVERY FROM DILUTE EXHAUST BY DIRECT CVS INJECTION OF 1.0 PERCENT NH_3 DURING THE HOT FTP DRIVING CYCLE

Test	Nominal Flow Rate (ft^3/min)		NH_3 Injected		NH_3 Recovered		Calculated amount of NH_3 recovered (ppm)[a]	Percent Recovery
	NH_3	CVS	Volume NH_3 injected (ft^3)[b]	Concentration NH_3 injected (ppm)	Total Diluted Volume (ft^3)[b]	Sample Concentration (ppm NH_3)[c]		
1	0.25	319	5.789	9791	7301	3.19	7.76	41.1
2	0.26	319	5.918	9791	7303	4.33	7.93	54.6
3	0.26	320	5.924	9791	7311	4.93	7.93	62.2

[a] This concentration representing 100 percent recovery, was obtained by back calculating from recovered sample concentration and percent recovery.

[b] Volume corrected to 1atm pressure and 68°F.

[c] Includes baseline correction.

motive exhaust samples.

The sampling parameters providing the most efficient collection of ammonia were selected. Twenty-five militers of the abosrobing solution, 0.01N H_2SO_4, is placed in each of the two bubblers in series and maintained at ice bath temperatures. Over 99 percent of the ammonia in the dilute exhaust flowing at 2 ℓ/min is captured in these two bubblers. The heated sample line (150-170 °F) vaporized moisture that may retain ammonia. After sample collection it is necessary to set instrument parameters to obtain good separation in the shortest time possible. These parameters, such as eluent concentration and flowrate, will depend on the particular column set in use. A 6 × 250 mm separator column has been found to resolve ammonia adequately. The 3 × 150 mm precolumn removes particulate, and the 9 × 250 mm suppressor column neutralizes the acidic eluent. With these columns installed, the eluent, 0.0075N HNO_3, flowing at 30 percent of pump capacity, gives good ammonia resolution. A small sample loop (100 μl) is necessary to prevent the very broad H^+ peak from the acidic absorbing solution from obliterating the ammonia signal. The injection variability of the ion chromatograph is 3.0 percent, and for standard preparation the variation is 1.5 percent. The ion chromatograph gives a linear response for $(NH_4)_2SO_4$ standards in the range 0.4 to 30 $\frac{\mu g\ NH_4^+}{m\ell}$, however, the attenuator is not linear between different sensitivity settings. Therefore, a different set of standards needs to be run at each attenuation. The study conducted on the effect of age on sample and standard stability showed the lifetime to be between four and five weeks. Thereafter, sharp jumps in concentration of ammonia occur. The results of the qualification tests show that the test car, a non-catalyst 1972 Plymouth equipped with a 360 V8 engine, yields 0.07 ppm NH_3 as a baseline emission level. A constant value was not obtained from either test in the recovery of ammonia injected into the exhuast of the test car during the FTP hot driving cycle. Results from both injections (0.1 percent and 1 percent NH_3) show increases in ammonia recoveries with successive testing. This trend can be explained by the fact that ammonia, an alkaline gas, is attracted to the metal in the CVS, the initial injection of ammonia served mainly to coat the inside of the CVS. Large portions of the second and third tests were also lost. Additional injections would probably show the same increasing trend. Following a similar injection into the CVS alone, 65 percent of the ammonia was recovered. The loss can also be attributed to the coating of the CVS tunnel. Removal of 85 to 94 percent of the ammonia remaining in the CVS requires running of the constant volume sampler alone for an hour to an hour and a half. Further running of the CVS yields no additional ammonia.

The ion chromatographic method measuring ammonia is an effective and efficient means of ammonia analysis in dilute automotive exhaust. This procedure is insensitive to most of the interferences plaguing other widely used methods. The ion chromatograph simplifies ammonia measurements to a one step injection, avoiding intermediate processes such as distillation, color development, or reagent preparation. The lengthiest portion of ammonia determination is the actual analysis time. This 12-20 minute analysis is relatively short for such a sensitive method (minimum detection limit is 0.01 ppm NH_3). Sample and standard stability as well as linearity of response in the concentration range of interest are additional factors which make this procedure the most desirable method of measuring ammonia in automotive exhaust.

SECTION 12

RESULTS AND CONCLUSIONS

To determine the suitability of the analytical procedures selected in Task I for dilute exhaust analysis, validation and qualification experiments were carried out. The validation experiments determined if the sampling and instrument parameters were appropriate for the quantitative analysis of dilute exhaust. The qualification experiments determined if the compounds of interest could be quantitatively recovered from the CVS tunnel with and without the presence of exhaust in the tunnel. The analytical procedures to be used in this project are listed in Table 58 along with methods of sampling and analysis. Table 58 also lists the validation and qualification experiments that were carried out.

The sampling parameters for all procedures were found to be adequate for the collection of each of the unregulated emissions. All samples, with the exception of the organic sulfides, nickel carbonyl, and hydrogen sulfide are stable for several days and can be stored and rerun at a later date. Hydrogen sulfide and organic sulfide samples must be run within hours after sampling, and nickel carbonyl must be run as soon after sampling as possible to prevent loss of sample integrity. All instruments demonstrate linearity of response for expected concemtration ranges (sample concentrations above the linear range must be diluted to concentrations that fall within the linear range of the instrument). The organic sulfides must be monitored carefully as traps containing over 200 ng of sample fall beyond the linear range of the FPD. The sample flow rate can be lowered to prevent overloading the Tenax trap. Test-to-test repeatabilities for all procedures are documented in this report. In most cases, repeatability is difficult to obtain at the lower concentrations, while the repeatability at high concentrations is easily obtained. Interferemces were checked and documented for each procedure. Phthalates were found to interfere with the aldehyde and ketone procedure and may cause erroneous results for crotonaldehyde. Nitric oxide is an interference in the nickel carbonyl procedure. Nitric oxide must be analyzed for separately and the results used to document the nickel carbonyl results. In the hydrogen sulfide procedure, sulfur dioxide decreases the apparent hydrogen sulfide concentration, and its presence or absence must be recorded. The other procedures have interferences that can be avoided if care is taken.

Qualification experiments were carried out on the aldehyde and ketone, organic amine, sulfur dioxide, nitrous oxide, hydrogen sulfide, total cyanide, organic sulfide, and ammonia procedures to determine the recovery of known amounts of each pollutant from the CVS tunnel with and without exhaust. Aldehydes and ketones, sulfur dioxide and nitrous oxide can be

TABLE 58. ANALYTICAL PROCEDURES FOR EMISSIONS CHARACTERIZATION

Compounds	Sampling	Analysis	Validation	Qualification
Aldehydes and Ketones	Impingers	DNPH	Yes	Yes
Organic Amines	Impingers	GC-NPD	Yes	Yes
Sulfur Dioxide	Impingers	Ion Chrom.	Yes	Yes
Nitrous Oxide	Bags	GC-ECD	Yes	Yes
Individual Hydrocarbons	Bags	GC-FID	Yes	Not required
Hydrogen Sulfide	Impingers	Meth. Blue	Yes	Yes
Hydrogen Cyanide + Cyanogen	Impingers	GC-ECD	Yes	Yes
Carbonly Sulfide + Organic Sulfides	Traps	GC-FPD	Yes	Yes
Nickel Carbonyl	Bags	CL	Yes	Not required
Ammonia	Impingers	Ion Chrom.	Yes	Yes
Sulfate	Filters	BCA	Not required	Not required
DMNA	Traps	GC-MS @ RTI	Not required	Not required

recovered quantitatively from the CVS tunnel with and without exhaust. There is a 10 percent loss of hydrogen sulfide and hydrogen cyanide in the presence of exhaust. The organic amines, ammonia, and the organic sulfides experience significant losses in the CVS tunnel with and without exhaust. These losses must be taken into account when determining the concentration of these compounds in exhaust.

The procedures discussed in this report are effective in collecting and analyzing dilute exhaust samples and are recommended for use in Task III of this report.

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APPENDIX A

INTERIM REPORT

TASK I

INTERIM REPORT

Task I

Selection of Analytical Methodology

This report is a summary of the results of the literature search and communications with EPA and industry researchers. A literature search for analytical methods was conducted on each compound (or group of similar compounds) and these results are presented in this report. A summary of the sampling and analysis procedures that are proposed for Task II is presented in Table 1. The compounds under study are described and the results of the literature search are detailed, in the following sections:

TABLE 1. PROPOSED SAMPLING AND ANALYSIS METHODOLOGY FOR EMISSIONS CHARACTERIZATION

	Proposed Analytical Methodology	
Exhaust Species	Sampling	Analysis
HCN	CVS Bag	GC-NPD
C_2N_2	CVS Bag	GC-NPD
N_2O	CVS Bag	GC-ECD
NH_3	Continuous into Impingers	Ion Chromatograph
Organic Amines	Continuous into Impingers	GC-NPD
DMNA	Continuous onto Trap	GC-CL w/MS Confirmation
SO_2	Continuous into Impingers	Ion Chromatograph
H_2S	Continuous into Impingers	Methylene Blue
COS	Continuous onto Trap	GC-FPD
CH_3SCH_3	Continuous onto Trap	GC-FPD
CH_3SSCH_3	Continuous onto Trap	GC-FPD
$C_2H_5SC_2H_5$	Continuous onto Trap	GC-FPD
Nickel Carbonyl	Continuous into Impingers	GC-ECD
H_2SO_4	Continuous onto Filter	BCA

Description	Page
I. Hydrogen Cyanide	3
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The following sections cover a general description of the exhaust species, results of the literature search, recommendations and a list of references for those compounds included in the emissions inventory.

I. Hydrogen Cyanide

A. General Description

Hydrogen cyanide is a colorless, flammable liquid with a characteristic odor of bitter almonds. The boiling point (1 atm) is 25.70°C and the melting point (1 atm) is -13.24°C.(1) The density of the liquid at 20°C is 0.6871 g/ml and the specific gravity of the gas at 31°C is 0.947.

Hydrogen cyanide vapor is highly toxic and in 1968 the American Conference of Governmental Industrial Hygienists recommended a threshold limit value of 10 ppm. This is the concentration in air to which nearly all workers may be exposed, day after day, without adverse effects.

B. Results of Literature Search

The analysis for HCN has been performed using three basic methods of analysis, wet chemical, specific ion electrode and gas chromatography. Prior to the advent of modern methods of instrumental analysis, a great portion of analytical chemistry was performed using classical wet chemical techniques. This was also true for the analysis for HCN where an analytical technique was developed for CN^-.(2) This technique was specific to CN but not specific to HCN. A number of years later, the approach presented by Epstein was applied to cigarette smoke and an automated system was developed.(3) Several years later the same authors expanded the technique to include aldehydes.(4)

This technique is commonly referred to as the "Pyridine-Pyrazolone" method and has been applied to automotive exhaust. Work has been performed by EPA and its subcontractors in the characterization of automotive exhaust for HCN. Although this procedure is generally considered to be specific for HCN, it is not and this will be discussed in more detail later in this section.

With the advancement of analytical technology, a technique utilizing potentiometric determination of CN^- was developed. This technique is commonly referred to as "Specific Ion Electrode" or "Ion Selective Electrode". During the past several years a number of articles have been published using the specific ion electrodes (SIE). These SIE are not specific to HCN but rather to CN^- and consequently most references are reporting CN^- rather than HCN. The SIE for measuring CN^- have been applied to water(5-11), air(12,13) and biological fluids.(14) Direct measurement using SIE would be extremely difficult in the concentration ranges that are anticipated. Previous experience with the Metrohm SIE indicate stability problems when working at continuous low levels.

This problem has been minimized by Burke(13) by incorporating a standard addition technique to bring the concentrations to the working range of the SIE. Although a satisfactory technique may be available that would allow measurement of CN^-, this may not be satisfactory for this research effort. During the literature search for cyanogen (C_2N_2) it was learned that C_2N_2 will hydrolize in an aqueous solution according to the equation(15)

$$C_2N_2 + H_2O \rightarrow HCN + HOCN$$

Since it is possible to form HCN from C_2N_2 in the presence of H_2O, an alternative method would be desired. Existing HCN procedures require collection in aqueous KOH or NaOH. This would assist in the artifact formation of HCN if C_2N_2 were present. An alternative approach would be to develop a technique that would measure both HCN and C_2N_2. This will be discussed later in this section.

The third approach to the analysis of HCN involves the use of a gas chromatograph. There have been several articles that have been published that are specific to the analysis of HCN. The original work was performed using thermal conductivity detectors and involved the use of HCN in the percent range.(16) Additional work was published by Isbell(17) regarding the separation of HCN and C_2N_2, but again at levels in the percent range. In 1975 Myerson and Chludzinski(18) reported better sensitivity using a gas chromatograph equipped with a flame ionization detector.

There are a number of important considerations that should be made regarding the analysis of HCN using gas chromatography. Hydrogen cyanide is reactive with any metal surfaces that it contacts, forming stable cyanide complexes. This type of problem is not apparent when working with high concentrations of HCN. Work is currently in Progress under EPA Contract 68-03-2499 regarding the gas chromatograph analysis for HCN. Although this work has not been completed, a satisfactory separation of HCN and C_2N_2 was obtained with a reasonable analysis time.

C. Recommendations for Analysis

Of the three techniques presented in the literature search, only analysis by gas chromatography will provide an analysis that is specific for HCN. In view of the fact that cyanogen is of interest to this research effort, it would be desirable to analyze these two species in the same procedure. The separation of HCN and C_2N_2 at low levels using gas chromatography (NPD) should be considered only a starting point. A number of experiments regarding stability, reactivity, etc., will be required to fully document this procedure. This technique involves direct sample injection via a gas-tight glass syringe. In order to insure sample integrity all gas chromatograph components that come in contact with the sample should be constructed of glass or teflon. This includes a glass-lined injector port, glass column, and glass-lined tubing in the detector interface.

At this time it is uncertain as to the minimum detection limit of the NPD, but it is expected to be less than 0.1 ppm on a direct injection. During the validation of the analytical methodology this will be determined and reported. Calibration blends of HCN and C_2N_2 are currently in hand to assist in any experiments that are necessary to validate the methodology. It should be noted that although the gas chromatograph procedure is specific to HCN a number of experiments will be required to insure there are no interferences from other combustion products that are known to be present in exhaust.

If the experiments designed to validate the analytical methodology indicate that there are problems with this approach, then another method will be recommended. If the gas chromatograph procedure is not satisfactory and HCN and C_2N_2 can not be measured separately, then it is proposed to combine the two and report them as CN^-. However, rather than using some of the aforementioned manpower intensive techniques, it is proposed to use another gas chromatograph method.(19) This involves the collection in aqueous KOH followed by extraction with hexane and reaction with Chloramine T to produce cyanogen chloride. An aliquot of the cyanogen chloride in hexane is injected into a gas chromatograph with an electron capture detector. This technique would provide adequate sensitivity but would not separate HCN and C_2N_2 but rather combine the two and report HCN and C_2N_2 as CN^-.

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II. Cyanogen

A. General Description(20)

Cyanogen is a colorless, flammable toxic gas at room temperature and atmospheric pressure with a characteristic almond-type odor. Cyanogen is a highly posionous gas, having a toxicity comparable to that of hydrogen cyanide. The freezing point (1 atm) of cyanogen is -27.9°C and the boiling point (1 atm) is -21.17°C. The chemical formula for cyanogen is C_2N_2

and it has a molecular weight of 52.04. Synonyms for cyanogen include dicyan and oxalonitrile. The 1968 American Conference of Governmental Industrial Hygienists has tentatively proposed a threshold limit value of 10 ppm for cyanogen.

B. Results of Literature Search

Upon conducting the literature search for analytical methods for measuring cyanogen, it became apparent that very little work has been published in that area. The analysis of cyanogen has been performed using gas chromatography.(17,21) In both instances, the analysis was carried out using laboratory blends of C_2N_2 with other gases. A thermal conductivity detector was used and the analysis was performed with cyanogen concentrations in the percent range. Although these publications are somewhat outdated, they will provide an initial starting point.

The past several years has seen a rapid development in gas chromatograph specialty detectors. The majority of work that was performed years ago was limited to thermal conductivity and flame ionization detectors. Recently, a Nitrogen-Phosphorus Detector (NPD) was developed by Perkin-Elmer and would be considered a prime candidate for performing trace analysis on nitrogen compounds such as cyanogen.

Work is currently in progress on EPA Contract 68-03-2499 to investigate the use of gas chromatography as an analytical technique for measuring HCN.(22) In this work, a cursory look at C_2N_2 is also being included. A Perkin-Elmer Model 3920B gas chromatograph equipped with a NPD is used to measure HCN and C_2N_2. Although this work is only in the preliminary stages, it appears that it may be possible to determine HCN and C_2N_2 in the same analysis.

Cyanogen will readily form HCN and HOCN when absorbed (15) in an aqueous solution so wet collection techniques will not be considered. The only apparent alternative is to measure a direct gaseous sample if C_2N_2 is to be measured separately. A number of experiments would be required to validate the sample integrity if this approach is used.

C. Recommendations

The most promising technique for the analysis of C_2N_2 appears to be the use of gas chromatography. A Perkin-Elmer 3920B with all glass components is available for this analysis. This unit has sub-ambient temperature capability as well as a NPD. Several preliminary experiments have been conducted that indicate HCN and C_2N_2 can be separated at reasonable temperatures. These experiments were conducted using nominal HCN and C_2N_2 concentrations less than 5 ppm. Although there are a substantial number of validation experiments that are necessary before this technique would be acceptable, it appears to have the most promise.

Several experiments that are planned include interferences from regulated emissions, sample stability, recovery, sample injection, etc. All of these will be part of the methodology validation in Task II and reported in subsequent progress reports. During the course of the methodology development, if it appears that there are problems with the proposed technique then an alternative method will be selected.

If cyanogen cannot be measured directly using gas chromatography then it is proposed to combine the analysis of HCN and C_2N_2 and determine them as CN^-. A basic absorbing solution would be used to collect these exhaust species during the emissions test. The basic solution is extracted with hexane containing chloramine T. The CN^- reacts with the Chloramine T and produces cyanogen chloride. The cyanogen chloride is then quantitatively determined using a gas chromatograph equipped with an electron capture detector (ECD).(19)

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III. Nitrous Oxide

A. General Description(23)

Nitrous oxide is a colorless, nonflammable gas with a slightly sweetish taste and odor. Nitrous oxide is nontoxic and nonirritating and is extensively used as an anesthetic in medicine and dentistry. The freezing point (1 atm) of nitrous oxide is -90.84°C and the boiling point (1 atm) is -89.5°C. The chemical formula for nitrous oxide is N_2O and the molecular weight is 44.013. Common synonyms for nitrous oxide are dinitrogen monoxide and laughing gas.

B. Results of Literature Search

The measurement of nitrous oxide has been performed by several researchers using gas chromatography.(24-28a) Most of this data was published during the early development of gas chromatography and consequently was not concerned with trace analysis. This work was conducted using a thermal conductivity detector and the minimum detection limits were quite high at that time. The nontoxic nature of the gas apparently precluded the development of analytical techniques for trace quantities. During the past several months, work has been performed at EPA-RTP in the development of a method to measure N_2O directly using a gas chromatograph equipped with an electron capture detector.(29) This analytical procedure has been applied to dilute automotive exhaust and provides the necessary sensitivity for this research effort. La Hue, et al(30), described a method for the measurement of atmospheric N_2O in the 250-300 ppb range. A concentration technique involving the use of molecular seive 5A trap is described. Upstream of the trap, water vapor and carbon dioxide are removed by passage of the air over anhydrous calcium sulfate and ascarite. The N_2O is desorbed using a water saturated helium stream. The water-displaced N_2O is then trapped on a silica gel column at -76°C. The silica gel column is heated to transfer the N_2O into a gas chromatograph for analysis.

C. Recommendations

It is recommended that the analysis of N_2O be conducted using a gas chromatograph equipped with an ECD. A Perkin-Elmer Model 3920B gas chromatograph with an ECD is available for this analysis. The GC operating conditions have been obtained from the Project Officer and a system for the measurement of N_2O has been assembled. The calibration of the instrument will be performed using N_2O in N_2 calibration blends. A Hewlett-Packard 3354 is available for data acquisition as needed. Since this method has been successfully applied to automotive exhaust, it is not anticipated that a significant effort will be required in the procedural development but rather to the validation of the entire system.

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IV. Ammonia

A. General Description(31)

Ammonia is a colorless, alkaline gas having a pungent odor. Ammonia readily dissolves in water. The freezing point (1 atm) of ammonia is -77.7°C and the boiling point (1 atm) is -33.35°C. The chemical formula for ammonia is NH_3 and the molecular weight is 17.031. The 1968 American Conference of Governmental Industrial Hygienists has recommended a threshold limit value of 50 ppm. This is the concentration in air to which nearly all workers may be repeatedly exposed, day after day, without adverse effects.

B. Results of Literature Search

The measurement of ammonia has been accomplished by a wide variety of techniques. Ammonia has been determined by such classical titrimetry methods as acidimetrity(32-41), complexometry(42), oxidimetry(43,44), and formal titration.(45-47) Although these methods may be satisfactory for specific applications, there are a number of factors which preclude their consideration as a method for this research effort. In general, titrimetry is limited to 10^{-4} M solutions and is reported to have a substantial number of interferences.

Gravimetric methods have been successfully used for the measurement of ammonia in several cases.(48-51) Generally speaking, if measurement of trace quantities of given species is required, gravimetric techniques are not adequately sensitive. The limited sampling time would eliminate any further consideration of gravimetric techniques for the measurement of ammonia. Gasometric methods have been used in determining high concentrations of ammonia.(52-54)

A number of instrumental optical methods have been applied to the measurement of ammonia. These methods include Nessler Reagent(55-57), Pyridine-Pyrazolone(58,59), Indophenol(60,61), Chloramine(62), Cupri-Ammonia complex(42), Ninhydrin(63), and Indirect Colorimetric Methods.(64) The direct spectrophotometric measurement of ammonia in air has been accomplished using ultraviolet(65,66), and infrared.(67,68) The use of electroanalytical methods has been applied to the measurement of ammonia in simple systems. The electrochemical techniques include polarography amperometry(72,73), coulometry(74-79), and conductivity.(80) Both gas(81,82) and paper(83) chromatography have been applied to the analysis of ammonia. The GC analysis(53) achieved a clean separation between ammonia and the lower molecular weight amines.

More recent advances in the measurement of NH_3 in trace quantities have involved specific ion electrode techniques. These techniques have included a wide variety of applications.(83-91) Although the specific ion electrode technique has distinct advantages over other methods, it does have certain limitations, namely instability at the low concentrations. With that in mind, consideration was given to several other alternative methods.

In 1973, Sigsby,et at, published results of work that employed the use of a chemiluminescent detector to continuously measure NO, NO_2 and NH_3 in dilute automotive exhaust.(92) It may be possible to modify this approach to remove the acid gases (NO and NO_2) and measure the NH_3 continuously. Ammonia has been quantitatively measured in dilute automotive exhaust(93) using an ion chromatograph. This procedure is free from many of the common interferences that plague the classical methods. The analysis time required for this analysis is less than 10 minutes and makes it a prime candidate for ammonia analysis.

C. Recommendation

The most promising technique for the measurement of trace quantities of ammonia in dilute automotive exhaust is by use of the ion chromatograph. This method involves the collection of ammonia in impingers using dilute H_2SO_4 as the absorbing reagent. Once the sample has been collected, an aliquot is injected into the ion chromatograph and the peak area is proportional to the concentration. This measurement method is the most straightforward of the techniques presented in the literature and probably gives the best results.

An alternative to this technique would be a modification of the system proposed by Sigsby, et al. An acid scrubber could be incorporated to remove the NO and NO_2 and allow measurement of NH_3 only. With the appropriate modifications, this could be incorporated into a gas chromatograph and a single bag sample could be used in lieu of continuous sampling. Both of these approaches would require a substantial amount of effort to validate the analytical methodology.

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V. Organic Amines

A. General Description(94,95)

The individual amines that are included in this analysis are monomethylamine, dimethylamine, monoethylamine, trimethylamine, diethylamine and triethylamine. The chemical formulas, molecular weights, boiling points, freezing points and synonyms for these low molecular weight aliphatic amines are presented in Table 2. In general, these amines have a fish-type odor at lower concentrations but more of an ammoniacal odor at higher levels. The 1968 American Conference of Governmental Industrial Hygienists has recommended a threshold limit value of 10 ppm.

TABLE 2. LIST OF INDIVIDUAL ORGANIC AMINES INCLUDED IN THE EMISSIONS CHARACTERIZATION INVENTORY

Name	Carbon No.	Chemical Formula	Molecular Weight	Boiling Point, °C	Freezing Point, °C	Synonyms
Monomethylamine (94)	1	CH_3NH_2	31.058	-6.32	-93.5	Methylamine, aminomethane
Monoethylamine (94)	2	$C_2H_5NH_2$	45.085	16.58	-81.0	Ethylamine, aminoethane
Dimethylamine (94)	2	$(CH_3)_2NH$	45.085	6.88	-92.19	none
Trimethylamine (95)	3	$(CH_3)_3N$	59.112	2.87	-117.08	none
Diethylamine (95)	4	$(C_2H_5)_2NH$	73.14	56.3	-50.	none
Triethylamine (95)	6	$(C_2H_5)_3N$	101.19	89.3	-114.7	none

B. Results of Literature Search

The measurement of individual low molecular weight amines has been conducted using a variety of gas chromatograph techniques. Hoshika(96,97) reported gas chromatographic separation of lower aliphatic amines in the free form and as their Schiff base derivatives. A glass column was employed to provide a separation of 11 amines using temperature programming and a thermal conductivity detector. This work was oriented toward achieving a satisfactory separation rather than being concerned with minimum detection limits. Sze(98) et al reported separation of methyl amines, ammonia, and methanol using a mixture of tetrahydroxyethylethylenediamine and tetraethylenepentamine. This work was expanded to include a total of 10 aliphatic amines. O'Donnell and Mann(99) used Dowfax 9N9, Carbowax 400 and Carbowax 20M to separate mixtures of aliphatic amines, aromatic amines and aliphatic amides. This work was performed using synthetic blends on a gas chromatograph with a thermal conductivity detector. McCurdy and Meiser(100) used a gas chromatograph with a flame ionization detector to determine fatty amines in trace quantities. The fatty amines were converted to trifluoroacetyl derivatives providing a sensitivity of 0.05 ppm fatty amine in water.

Smith and Waddington(101) used aromatic polymer beads to separate a wide range of aliphatic amines. Peak tailing was found to exist because of two types of active sites on the polymer: simple acidic sites which can be neutralized by treatment with base, and metal ions which must be deactivated by addition of an involatile complexing agent. Glass columns were used in a gas chromatograph with a flame ionization detector. Synthetic blends ranging from C_1-C_6 were separated and analyzed using this approach. Carbopak B/4% Carbowax 20M/0.8% KOH(102) and 28% Pennwalt 223/4% KOH(103) have been reported to give satisfactory separations of lower aliphatic amines.

Analysis of amines as derivatives has been shown to be a valuable analytical tool to determine trace quantities.(104) Thirteen different derivatives were evaluated in terms of FID and ECD response characteristics. This work was limited to primary amines and under optimum conditions amines down to 10 picograms could easily be quantified using an ECD detector. Clark and Wilk(105) used an ECD to evaluate the properties of halogenated amine derivatives. No increase in the sensitivity for the trifluoroacetyl amine derivatives using ECD was observed.

Mosier(106) et al, quantitatively measured aliphatic amines volatilized from cattle feedyards. Direct gas chromatograph injection of the acid solutions and GC separation of the pentafluorobenzoyl derivatives of the malodorous volatiles were used in identification. The derivatized amines were analyzed using a gas chromatograph equipped with an electron capture detector. The two columns used in this work were 6% DEGS and 10% Igepal CO 880.

Methylamine and ethylamine were detected in irradiated beef by Burks(107), et al. Several techniques including colorimetric paper chromatography and gas chromatography were used in quantifying results. Gas chromatographic determination of free mono-, di-, and trimethylamines in biological fluids was performed by Dunn(108), et al. A flame ionization detector was used to quantitatively separate the lower aliphatic amines. Separation of mono-, di-, and trimethylamine from extracts of fish tissue was achieved by Gruger.(109)

Andre(110) et al developed a precolumn inlet system for the gas chromatographic analysis of trace quantities of short-chain aliphatic amines. Losses inherent in the collection and direct gas chromatograph analysis of field air samples containing volatile amines necessitated an indirect analytical scheme. A teflon tube (3" x 5/16" OD) was filled with 20/30 mesh Ascarite and placed in the injector inlet of the gas chromatograph. Samples were collected in dilute H_2SO_4 and aliquots were injected into the pre-column of the GC. Release of the free amines was found to be sufficiently reproducible for quantification of results. This technique avoided the problems encountered by Umbreit(111) et al, and Hardy(112) when using base loaded columns to analyze acidified aqueous solutions of amines from fish. The in situ release of the free amines from their salts produced a chromatographic column that changed with every injection. In addition, the column had a very short usable lifetime and lacked reproducibility after extended use.

Bowen(113) described a gas chromatograph procedure for the analysis of aromatic amines using an adsorption technique. Quantitative adsorption and desorption of aromatic amines using Tenax GC was demonstrated at the nanogram level. Samples were pulled through the Tenax GC trap for specific sampling periods, thermally desorbed at 250°C and analyzed in a GC with a FID. The author recommended use of a NPD to increase sensitivity for aromatic amines on the tail of hydrocarbon solvents and eliminate venting the solvent.

C. Recommendations

The analysis for individual aliphatic amines should be conducted using gas chromatography. Of the specialty detectors available for the analysis of nitrogen compounds the NPD is a prime candidate as a detection method. Sample collection in dilute H_2SO_4 into an all glass system with an ascarite pre-column would provide satisfactory sample acquisition and analysis in a reasonable analysis time. A Perkin-Elmer 3920B gas chromatograph equipped with a NPD and an all glass system is available for this analysis. Subambient temperature capability is available if necessary and a Hewlett-Packard 3354 computer system will be used for data acquisition.

An alternative approach would be to convert the amines to fluoro-containing derivatives and measure the derivatives using a GC with an ECD. Sample collection would be made by using impingers, as with the aforementioned approach. A third approach would be to use direct gas injection from a bag sample collected during a driving cycle. It is uncertain as to the feasibility of using a Tenax GC trap as a collection technique for low molecular weight aliphatic amines. The low freezing point of these compounds may be too low to quantitatively concentrate on the Tenax GC traps.

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VI. N-nitrosodimethylamine(114,115)

A. General Description

N-nitrosodimethylamine is a yellow liquid at room temperature boiling at 152°C. It has a chemical formula of $(CH_3)_2NNO$ and a molecular weight of 74.08. It is very soluble in water, alcohol and ether. N-nitrosodimethylamine has caused fatal poisoning, severe liver injury and is suspected of being a carcinogen. Common synonyms include dimethylnitrosoamine, dimethyl N-nitrosoamine and nitrous dimethylamide.

B. Results of Literature Search

In 1956, Magee and Barnes(116) reported that dimethylnitrosoamine (DMNA) caused malignant tumors in rats. Lijinsky and Epstein(117) identified N-nitroso compounds as a major class of carcinogens that may be related to human cancer. Magee and Barnes(118) reported that 75 of 100 N-nitroso compounds tested were shown to be carcinogenic. Koppang and Rimslatter(119) presented results documenting the toxic and carcinogenic effects of DMNA on rodents. In 1971, Magee(120) presented additional data to substantiate the carcinogenic effects of N-nitroso compounds. The potency of DMNA as a carcinogen has been repeatedly demonstrated in experimental studies on mice, hamsters , guineas pigs, rats, rabbits and several species of fish.(121)

Standard analytical methods for N-nitroso compounds were originally based on gas chromatography but were available for only volatile compounds.(122-129) These procedures were lengthy and time consuming and required an extensive sample clean up prior to sample concentration and analysis by gas chromatography. Potential interferences must be removed when using the nitrogen specific alkali flame ionization and the Coulson electrolytic conductivity detectors. Sen(130) and Althorpe(131), et al converted the nitrosamines to a nitramine and used a gas chromatograph with an electron capture for quantitative measurement. Allison(132) used a GC-ECD system to measure polyfluorinated amide derivatives of various nitrosamines. Most GC methods relied on steam volatilization or vacuum distillation as the primary purification and concentration technique. Subsequently, all available data was limited to volatile nitrosamines.

In 1974, Fine(133) et al introduced a specific method of detection for a variety of nitrosamines. This instrument is commercially available from Thermo Electron Corporation and is called Thermal Energy Analysis (TEA). The TEA uses a selective catalyst to cleave N-nitroso compounds, splitting off the nitrosyl radical. The nitrosyl radical passes through a cold trap (-150°C) to the reaction chamber where it reacts with ozone, giving nitrogen dioxide in the excited state. The light emitted from the excited state nitrogen dioxide returning to the ground state is measured in the near infrared region of the spectrum. Although some data is available on interfering species, a substantial effort would be necessary before satisfactory application of the TEA to automotive exhaust could be considered.

The TEA is sensitive to picogram quantities with a linear range extending over five orders of magnitude.(134) The TEA has been interfaced to both a gas chromatograph(135) and more recently, a high pressure liquid chromatograph.(136, 137) Although the TEA is extremely sensitive and selective, sample cleanup procedures are necessary.(138) Once the instrument had been sufficiently developed, the TEA was applied to a wide variety of sources.(139-148b)

Pellizzarihas applied a gas chromatograph-mass spectrometer system to identify DMNA in ambient air.(149) This technique concentrates the organic vapors in glass cartridges filled with specially preconditioned Tenax GC.(150-155) DMNA recovery was accomplished by thermal desorption and analyzed using GC-MS using capillary glass SCOT columns. Identification of DMNA was confirmed by comparison of its mass spectrum with that of pure N-nitrosodimethylamine. The retention times of the unknown and pure compound were identical on three different columns. The advantage of this approach is the identification using GC-MS; whereas the TEA does not provide absolute identification.

In 1975, a comparison of the two techniques was possible by comparing the results of ambient air samples in Baltimore, Md.(156) Parallel analyses were conducted using different collection and analysis procedures. The samples were collected over a three month period and involved a number of industrial locations. The TEA analysis was performed by a team of researchers from Thermo Electron Corporation. Samples were collected cryogenically and analyzed on a TEA Model 502. The second set of researchers was headed by Pellizzari of Research Triangle Institute. Their samples were collected on Tenax GC cartridges, thermally desorbed and resolved by capillary gas chromatography. The mass cracking patterns were continuously and automatically obtained throughout the GC run with a Varian-MAT CH-7 GC-MS computer system. Identification of DMNA was achieved by comparing the mass cracking pattern to an eight major peak index (157, 158), with supplementary confirmation by comparing with known DMNA retention times on two different capillary columns.

At the Food Manufacturing Corporation (FMC) location, additional samples were collected by FMC researchers.(159) These independent cold trap GC-MS experiments conducted by the FMC analytical team also confirmed the presence of DMNA in the air on the FMC property. At the duPont location, independent cold trap GC-MS experiments were carried out by a duPont analytical team, and the results agreed within an order of magnitude.(160)

Several experiments were conducted to validate that DMNA was not formed either during collection or analysis.(156) For the cryogenic procedure, DMNA was not detected when dimethylamine and $NO_x(NaNO_2)$ was added to the trap. In the field work, an increase in DMNA above background levels was not observed, even with a thousandfold excess of dimethylamine. The possibility of DMNA formation on the Tenax cartridges was investigated both in the laboratory and in the field. Enhancement of DMNA was not observed above the background when dimethylamine was preloaded into the Tenax cartridge. No DMNA was detected when moist air containing $NO+NO_x$ (1:1) was drawn across a permeation tube containing dimethylamine and into the Tenax cartridge.

Since both approaches have demonstrated that the DMNA reported was not as a result of artifact formation, it is of interest to compare the results on parallel samples.(156) The agreement between the two techniques should only be considered fair. At the high levels (32,000 μg/m^3) the agreement was generally within a factor of three. At the lower levels (500 μg/m^3), the agreement between the two techniques deteriorated on several samples and was only fair on the remaining samples.

C. Recommendations

It is recommended to use an analytical system, such as the TEA or an equivalent system for the measurement of DMNA in exhaust. In addition, validation of the sampling and analysis methodology would be performed with supplemental GC-MS analysis. It is anticipated that the GC-MS analysis would be conducted by Dr. Edo Pellizzari of Research Triangle Institute during Task II. If it is not feasible to obtain or develop a system similar to that developed by Dr. David Fines, the alternative would be to collect the exhaust samples on Tenax GC and send them to RTI for DMNA analysis by GC-MS.

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VII. Sulfur Dioxide

A. General Description[161]

Sulfur dioxide is a highly irritating, nonflammable, colorless gas at room temperature and atmospheric pressure. The gas is readily detectable in concentrations of 3-5 ppm by the human nose. The freezing point (1 atm) is -75.5°C and the boiling point (1 atm) is -10.0°C. The chemical formula for sulfur dioxide is SO_2 and the molecular weight is 64.063. A common synonym for SO_2 is sulfurous acid anhydride.

B. Results of Literature Search

The bulk of published literature regarding the analysis of SO_2 has been in reference to ambient air sampling. During recent years, with the development of instrumental methods of analysis, SO_2 has been measured in stationary and mobile source exhausts. A review of the references shows a wide variety of analytical techniques. The most commonly employed colorimetric technique is the West-Gaeke method.(162-166) This method has been collaboratively tested, the lowest concentration range studied being well above the levels most frequently present in rural and global background air.(167) A modified version of the West-Gaeke method involves the collection of SO_2 in 0.1M sodium tetrachloromercurate (II) (TCM) to form a dichlorosulfitomercurate complex (DCSM). The DCSM resists oxidation by either oxygen in the air or that dissolved in the absorbing solution. Ethylenediamine tetracetic acid disodium salt (EDTA) is added to the TCM absorbing solution to complex any heavy metals that could oxidize sulfur dioxide before DCSM is complete.(168, 169) Sulfamic acid is added to destroy any nitrite ion in the absorbing solution.(170)

The colorimetric determination of sulfur dioxide,is based upon the measurement of the red-violet color produced by the reaction of DCSM with hydrochloric acid, pararosaniline and formaldehyde. Investigations into the effect of dye purity on the analytical procedure have been reported by several researchers.(171, 172) Techniques for purification of commercial grade dye by recrystallization have been published.(163, 165, 173) Pararosaniline purified especially for the colorimetric analysis of sulfur dioxide is commercially available.(173)

The major potential source of error associated with the West-Gaeke colorimetric method for measuring SO_2 is the widely differing collection efficiency reported for Greenburg-Smith and midget impingers at low atmospheric concentrations.(174) Urone et al investigated the collection efficiency in TCM solution of microgram quantities of sulfur dioxide tagged with ^{35}S.(175) It was found that series bubblers cannot be used to determine absorber collection efficiency. Boström observed a 99% collection efficiency for sulfur dioxide in TCM solution within the range of 100-1000 ppb.(176)

Work has been conducted in the development of other colorimetric methods for the analysis of sulfur dioxide. Attari absorbed sulfur dioxide into a solution of ferric ammonium chloride, perchloric acid and phenanthroline dye.(177) A color complex with an absorbance at 510 nm was formed and although the color developed within 10 minutes it tended to fade with time. Hydrogen sulfide was observed to seriously interfere.

Kawai used the reaction of barium chloranilate with sulfate as an indirect measurement of sulfur dioxide.(178) Sulfur dioxide was absorbed in a solution containing hydrogen peroxide and barium chloranilate. Barium chloranilate reacts with the sulfate ion producing a red-violet chloranilic acid ion. Although this method may be satisfactory for flue gas analysis it lacks the sensitivity required for ambient air analyses.

Conductivity methods have been used for continuously monitoring sulfur dioxide in air.(179) The conductivity of a dilute sulfuric acid-hydrogen peroxide reagent changes due to the absorption of pollutants. This change in conductivity is assumed to result primarily from sulfur dioxide absorbed from the sampled air and oxidized to sulfuric acid. In many cases, sulfur dioxide is the major pollutant present; however, if other pollutants are present, their collection efficiency and solubility may be significantly different than for sulfur dioxide. Several field comparisons of conductivity with other sulfur dioxide procedures indicate a fair agreement.(180-185) Hydrochloric acid gas, ammonia and chlorine substantially increase conductivity. Shikiya and McPhee found two- to fourfold differences between different conductivity analyzers and between conductivity and colorimetric analyzers.(182) Although the conductivity procedure may be acceptable for point sources of sulfur dioxide in isolated areas, its high potential for positive and negative interferences limits its application.

Iodometric methods were among the first adapted for air pollution analysis from the industrial hygiene literature. With this method the sulfur dioxide is collected in an impinger containing a standard NaOH. The absorbing solution is acidified and the liberated sulfurous acid is titrated with standard iodine solution.(183) Another method employs a standard iodine-potassium absorbing solution.(184) Iodometric methods of analysis for sulfur dioxide generally suffer from a lack of sensitivity and interferences from H_2S.

Adsorption sampling methods have also been developed for the measurement of sulfur dioxide.(186) Sulfur dioxide is sorbed on silica gel, desorbed and reduced to H_2S at 700-900°C over a platinum catalyst. The H_2S is then absorbed in a 2% ammonium molybdate solution and determined colorimetrically. Although this technique is relatively specific for SO_2, the final colorimetric determination by the molybdenum complex does not utilize the most sensititive method available.

In addition to the aforementioned techniques, sulfur dioxide has been measured by filtration(187-191) and static collectors.(192 - 198) Air samples are passed through potassium bicarbonate impregnated filters and analyzed for sulfate. The collection efficiency of these filters is dependent upon humidity, temperature, and the atmospheric concentration of sulfur dioxide. The lead peroxide candle static collector was developed by Wilson and McConnell as an inexpensive method for measuring relative "sulfation" of the atmosphere.(192) The sulfur dioxide collection efficiency is dependent upon temperature, relative humidity, wind speed, atmospheric concentration of SO_2 and the length of exposure period.(193) Ikeda determined ambient SO2 levels by collecting samples on active carbon filters, washed with distilled water and titrated with barium chloranilate.

With the advent of modern instrumental methods of analysis, specifically gas and ion chromatography, a substantial amount of data has been published. Most trace gas analysis for SO_2 has been conducted using gas chromatographs with flame photometric detectors (FPD).(199 - 208) The FPD is highly selective for sulfur compounds and has low minimum detection limits. Analysis for SO_2 is generally performed using all teflon or glass systems. Sulfur dioxide will react with active sites in the gas chromatograph system, making the use of inert materials essential for trace quantitative analysis. Gas chromatographs with FPD and linearizing circuitry provide a wide dynamic range for ambient and source SO_2 levels. In some instances the collection technique precludes the use of GC-FPD techniques; i.e., bag sampling from dilute automotive exhaust or source sampling. The use of gas chromatography would be a prime candidate if the sample integrity could be assured in the sample acquisition and subsequent analysis.

A more recent development in methods of analysis for sulfur dioxide involves the use of ion chromatography.(209) This technique involves collection in a hydrogen peroxide absorbing reagent and measurement of the resulting sulfate ion using ion chromatography. Ion chromatography is a specialized area of liquid chromatography,which will separate and quantify the individual cations or anions. This technique has been applied to the measurement of SO_2 in ambient air and adaptation to dilute automotive exhaust should not be difficult.

Other instruments are commercially available that are reported to measure SO_2 in ambient or dilute automotive exhaust. Such instruments include continuous detection by pulsed fluorescent UV and second derivative UV analyzers. A pulsed fluorescent UV analyzer for SO_2 was found to give recoveries on the order of 115-125%, indicating that a positive interference is present.(210) The second derivative UV sulfur dioxide analyzer has inherent problems when being used on continuous samples. The mirrors are located in the actual cell and become coated with various exhaust components even after filtration of the sample. The mirrors will become etched and need resurfacing if the unit is used in the presence of SO_2, $SO_4^=$, or other corrosive exhaust components. The inherent noise level along with the consistent mirror problem preclude the use of a second derivative UV analyzer for measuring SO_2 on a continuous basis.

A variation of the GC method for measuring SO_2 is the use of a continuous analyzer using an FPD detector. Although this approach is good in theory, it has several problems associated with the performance of the FPD detector. These units were originally designed to monitor SO_2 levels in the ambient and adaptation to automotive exhaust was not straightforward. Air samples had essentially the same O_2 and N_2 levels all of the time; however, dilute exhaust samples have variable CO_2, O_2 and N_2 concentrations. The species have been found to cause quenching effects on a FPD detector. With the constantly changing CO_2, O_2 and N_2 it would be impossible to correct for any quenching effect. The use of a continuous FPD analyzer for measuring SO_2 in automotive exhaust would not be acceptable unless the quenching effects could be eliminated.

C. Recommendations

The method that appears the most appropriate for the measurement of SO_2 in dilute automotive exhaust is that using the ion chromatograph. This technique has been found to be accurate at ambient levels and could be readily adapted to exhaust samples. The sample is collected in hydrogen peroxide and an aliquot is injected into the ion chromatograph. The resulting $SO_4^=$ peak is proportional to the SO_2 concentration and emission rates can be determined.

An alternative procedure would be to use a modified West-Gaeke method. Although this procedure has been used for a number of years in ambient studies, the TCM absorbing reagent is quite dangerous and extreme care must be exercised during its handling.

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VIII. Hydrogen Sulfide

A. General Description(211,212)

Hydrogen sulfide, also called hydrosulfuric acid and sulfureted hydrogen has the chemical formula H_2S. This flammable, poisonous gas has the characteristic odor of rotten eggs. The boiling point (1 atm) is -60.33°C and the melting point (1 atm) is -85.49°C. The density of the liquid at the boiling point is 0.993 g/ml and the specific gravity of the gas at 15°C is 1.1895. Hydrogen sulfide is considered an extremely toxic gas. In 1968, the American Conference of Governmental Industrial Hygienists recommended a threshold limit of 10 ppm for workers exposed over long periods of time without adverse effects.

B. Results of Literature Search

Since hydrogen sulfide has such a terrible odor and is extremely poisonous, several methods have been developed for its detection. Some of these methods are plate, tiles, tapes or filters, catalysts, fluorimetry, infrared spectroscopy, sulfur ion selective electrode, gas chromatography, coulometry and two colorimetric methods.(213,214) Most of these methods are useful for specific situations; require long sampling times; are only useful at high concentrations; or are also sensitive to mercaptans, organic sulfides and sulfur dioxide and trioxide. Many of these species are present in the exhaust and would complicate the analysis.

The methods least likely to be advantageous are the tape, tile, plate and filter methods. These surfaces are coated with lead acetate or mercuric chloride.(215-218) A sheet of metallic silver has also been used. The problem with this technique is one of time. The sampling times are between 10-90 minutes for the mercuric chloride tape and seven days for the metallic silver plate. Hydrogen sulfide concentration is measured by the change in reflectance of the plates after exposure or the optical density (percent transmittance) of the tape. This method would be good for ambient air samples on a daily or hourly basis.

There are two methods using a catalyst to determine hydrogen sulfide concentration. The first method uses a nickel catalyst to reduce organic sulfides into hydrogen sulfide, which is analyzed with the methylene blue method discussed later.(219) The other method uses palladium.(220) This noble metal allows hydrogen to diffuse through the metal lattice. The rate of hydrogen transport is constant at a given temperature and pressure difference across the palladium foil. Hydrogen sulfide "poisons" the surface of the catalyst and inhibits the diffusion rate of hydrogen. This is used with "on line" systems and would be difficult and expensive to adapt for use with automotive exhaust.

The fluorimetry method uses fluorescein-mercuric acetate reagent.(221,222) Hydrogen sulfide quenches the fluorescence of this reagent. This method has a reported detection limit of one ppb. A study of the possible interferences from exhaust species has not been carried out and confirmation of the reported sensitivity is necessary.

The infrared method uses the principle of light absorption due to the vibrational modes of the molecule. This technique is sensitive to about 10 ppm but any sulfide or disulfide present will interfere. This is also a useful method for continuous monitoring of hydrogen sulfide levels.

The sulfur-ion selective electrode contains a solid silver sulfide membrane which separates the internal reference from the test solution.(223-227) A voltage develops between the test solution and the reference. This voltage depends on the activity of the silver ion. Previous experience with ion selective electrodes has shown stability problems at low concentrations.

Gas chromatography is a useful technique for separating and analyzing many compounds. Many different detectors and columns have been used to determine hydrogen sulfide. These have been used on ambient air samples and "on line" systems.(199-208,228-238) From preliminary tests, hydrogen sulfide is highly reactive with the species in automotive exhaust. In this case, it is difficult to preserve sample integrity. A method of trapping other than Tedlar bag samples would have to be found.

A coulometric microtitration device was adapted from gas chromatography to direct use on ambient air analysis and used by Adams et. al.(239) Filters were used to eliminate some of the sulfur-containing constituents in the sample. Coulometric detectors lack the selectivity required.(240)

There are two colorimetric methods available.(241-250) The sodium nitroprusside method is sensitive to about one ppm. The methylene blue method is sensitive to 1-3 ppb. Cadmium or zinc hydroxide, cadmium sulfate, or zinc acetate are used as the absorbing media in a glass impinger. An acidic solution of N,N-dimethyl-p-phenylenediamine dihydrochloride or sulfate is then added to the absorbed sample. Methylene blue is formed and fully developed after 15 minutes at 20°C. The color is constant in subdued light for several hours. The absorbance at 670 nm is determined with a spectrophotometer.

C. Recommendations for Analysis

Of the many techniques available from the literature search, the best appears to be the methylene blue method. The proposed procedure was obtained from the Project Officer under EPA Contract 68-03-2499 in May, 1977. This is a modification of the technique used by Gustafsson.(243) Although this method is well documented, tests will be run to determine concentration limits and possible interferences.

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IX. Organic Sulfides

A. General Description

Carbonyl sulfide, dimethyl sulfide, dimethyl disulfide, and diethyl sulfide are organic sulfides of concern on this research effort. The chemical formulas, molecular weights, freezing points, boiling points and common synonyms are listed in Table 3. Carbonyl sulfide is the only sulfide of interest that is a gas at room temperature. In general, the organic sulfides are malodorous compounds producing an unpleasant odor similar to rotten eggs. The 1968 American Conference of Governmental Industrial Hygienists made no recommendations for threshold limit values for these sulfides.

B. Results of Literature Search

Spencer(251) et al applied the use of gas chromatography to analyze gas odorants for mercaptan and sulfides. In earlier work, Sumner(252) et al and Liberti(253) et al had limited their studies to mercaptans in gas odorants. Ryce(254) et al and Desty (255)expanded the analysis of gas odorants to include sulfides, although no retention times were given. The aforementioned references used thermal conductivity detectors in their analyses and were not concerned with trace gas analysis.

Coleman(256), et al used gas chromatography and mass spectrometry to separate and identify eleven low-boiling sulfur compounds in crude oil. Other researchers were performing independent studies on the retention times under various gas chromatograph conditions.(257,258) Improved separation of mercaptans and sulfides using temperature programmed gas chromatography was reported by Sullivan(259), et al. Sullivan in effect, confirmed earlier work published by Dal Nogare(260) et al and Harrison(261) et al. Adams and Koppe(262) expanded the analysis to include hydrogen sulfide, sulfur dioxide, mercaptans, alkyl sulfides and disulfides. This work presented a gas chromatographic technique for the separation and identification of complex mixtures in Kraft pulp digester blow gas and black liquor combustion products.

TABLE 3. LIST OF SULFUR COMPOUNDS INCLUDED IN THE ANALYSIS OF ORGANIC SULFIDES

Sulfur Compound	Chemical Formula	Molecular Weight	Freezing Point, °C	Boiling Point, °C	Synonyms
Carbonyl Sulfide	COS	60.075	-138.8	-50.2	Carbon oxysulfide
Dimethyl Sulfide	CH_3SCH_3	62.13	-98.27	37.3	Methyl sulfide
Dimethyl Disulfide	CH_3SSCH_3	94.20	-84.72	109.7	none
Diethyl Sulfide	$C_2H_5SC_2H_5$	90.19	-103.9	92.1	Ethyl sulfide
Methyl Mercaptan	CH_3SH	48.11	-121.0	6.2	Methanethiol
Ethyl Mercaptan	C_2H_5SH	62.13	-144.4	35.0	Ethanethiol

Schols(263) quantitatively measured carbonyl sulfide in natural gas using gas chromatography. Although a minimum detection limit of 25 ppm COS was reported, propylene was found to interfere with the analysis. Hall(264) measured trace quantities of COS in carbonated beverages using a gas chromatograph equipped with an electron capture detector. An improved minimum detection limit of 0.3 ppm was a substantial improvement over the work reported by Schols.(263) Adams(265) et al applied absorption techniques to concentrate sulfur compounds in waste process gases. The pollutants were absorbed on activated silica gel at -78.5°C, desorbed under heat and vacuum, trapped at -196°C and transferred onto a gas chromatograph column for analysis.

In 1965, Feldstein(266) reported separation of a variety of sulfur compounds on a number of gas chromatograph columns. Several columns showed promise, but did not separate organic sulfur compounds from normally occurring atmospheric hydrocarbons. Fredricks and Harlow(267) quantitatively measured mercaptans in sour natural gas by gas chromatography and microcoulometry. Hydrocarbons did not interfere and the method was sensitive to as little as 1 ppm of individual mercaptan. The method required only 30 ml of sample but required one hour to complete the analysis.

With the development of the Melpar flame photometric detector, the detection limits of sulfur compounds were improved considerably. In 1970, Mizany(268) characterized the FPD response to several sulfur compounds and made comparisons to a Dohrmann microcoulometric detector. Stevens and O'Keeffe(203) discussed application of flame photometric detectors to air pollution monitoring low concentrations. Permeation calibration tubes were used to generate continuous samples of known concentrations for various sulfur compounds. Both continuous and grab sampling techniques were used in this study. Kummer(269) et al used the gas phase chemiluminescent reaction of ozone with a number of organic sulfides. The possible uses of these reactions in monitoring low concentrations of ozone and sulfur-containing pollutants were discussed.

In 1972, Rasmussen(270) used a gas chromatograph with a flame photometric detector to measure trace organic sulfur compounds in air. This procedure was also applied to soil and water analysis and was found to be a very sensitive and rugged instrument. The use of teflon tubing throughout the gas chromatograph system minimized adsorptive losses. Pecsar and Hartman(202) described an automated gas chromatographic analysis of sulfur pollutants. By employing an all teflon system, sensitives on the order of 10 ppb were achieved with confidence. Calibrations were made using permeation calibration tubes. Column fabrication techniques were discussed with methods for achieving optimum column and detector operation.

In 1974, Bremner and Banwart(208) used a Beckman GC-4 equipped with a Melpar flame photometric detector to identify volatile sulfur compounds. Several columns were evaluated at several temperatures and GC separation data is presented. Chromosorb T, Carbopak B-HT-100, Chromosil 310, and Deactigel were evaluated in teflon columns. A number of other researchers(271-277) employed gas chromatography to quantitatively measure various sulfur compounds from a wide variety of sources. Commercial analyzers are available that measure COS in the sub-ppm range.

C. Recommendations

Based on the results of the literature search, it is apparant that the only technique that can detect ppb range sulfur compounds requires the use of a gas chromatograph with a flame photometric detector. It is proposed to use a Perkin-Elmer gas chromatograph with a flame photometric detector. The organic sulfides will be concentrated on a Tenax-GC trap, thermally desorbed into the gas chromatograph and quantitatively measured using certified permeation calibration tubes as reference.

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X. Nickel Carbonyl

A. General Description(278,279)

Nickel carbonyl, also called nickel tetracarbonyl, is a colorless, flammable, highly volatile liquid. The melting point (1 atm) is -25°C and the boiling point (1 atm) is 43.2°C. The density of the liquid at 20°C is 1.310 g/ml.

Nickel carbonyl has a musty "damp cellar" or "sooty" odor.(280) It can be detected by the human olfactory at 1-3 ppm. In 1968, the

American Conference of Governmental Industrial Hygienists recommended a threshold limit for daily exposure without adverse effects of 0.001 ppm.

Carbon monoxide is a π-acceptor ligand.(281) It bonds by donating an electron from a sigma orbital and accepting an electron from a d π or dp π metal orbital. In the case of nickel carbonyl, the valence is zero and the structure is tetrahedral. Thermodynamic data show that it quickly decomposes.(282)

B. Results of Literature Search

The toxicity and flammability of nickel carbonyl have provided an impetus for the development of tests to determine concentrations. There are several methods available. Some of these are infrared spectroscopy, spark spectroscopy, flame photometry, light reflectance, colorimetry, and a gas chromatography method using an electron capture detector.

Infrared spectroscopy is reported to have a detection limit of four ppm by volume.(283) Spark spectroscopy has a 0.1 ppm detection limit but the exposure time of the photographic plate requires considerable time. The flame photometric method is expensive to operate and requires the use of an open flame.(284) The detection limit is 0.1 ppm.

McCarley et al (285) developed a device that takes advantage of the thermodynamics of nickel carbonyl. In the absence of carbon monoxide, nickel carbonyl decomposes on contact with a hot surface, in this case borosilicate glass. The rate of decomposition is proportional to the nickel carbonyl concentration. The intensity of plane-polarized light reflected from the surface is calibrated in ppm of nickel carbonyl. The detection limit is 0.05 ppm but it is also sensitive to iron carbonyl and possibly other metallo-organic gases. Another method used by Ball(286) et al also takes advantage of the thermodynamic properties. Nickel carbonyl is detected by its pyrolysis products on the gaseous conductance in an ionization chamber.

There are several colorimetric methods available for the determination of nickel carbonyl. The first uses a solution of iodine in ethanol or chloroform as the absorber. This technique was used by Kincaid et al(287) and Hunold and Pietrulla.(288) The nickel in the samples are complexed with dimethylglyoxime. The optical density is measured spectrophotometrically at 440 nm. The detection limit is 2 ppb but the collection time is on the order of hours. The second method involves a saturated solution of sulfur in trifluoroethylene.(289) The samples is examined spectrographically in the ultraviolet region of the spectrum. A third method involves the reaction of nickel carbonyl with red mercuric oxide at 200°C.(290) The liberated mercury is determined spectrographically. A fourth method uses dilute sulfuric acid to collect nickel carbonyl. Sodium diethyldithiocarbamate is used to complex the nickel. Belyakov(291) used chloramine B in ethanol as the absorber and complexed the nickel with dimethylgloxime. Vol'berg and Gerskhovich(292) used potassium iodide on silica gel as the absorber.

Iodine ion is released and measured colorimetrically. Another method uses dilute hydrochloric acid as the absorbing reagent and alphafurildioxime as the complexing agent. These last two seem questionable although Brief et al[293] reports a 90 percent collection efficiency with a 3 percent hydrochloric acid solution.

A gas chromatograph with a Carbowax 20 M column and an electron capture detector was employed by Sunderman et al (294) to determine nickel carbonyl in the blood and breath of rats. The technique involved vacuum extraction of nickel carbonyl from the blood and trapping in cold ethanol (-78°C). The electron capture detector is insensitive to most hydrocarbons but is sensitive to organo-metallic compounds.

C. Recommendations for Analysis

An adaptation of the gas chromatography method would seem the most likely candidate for the analysis of nickel carbonyl. Nickel carbonyl is highly soluble in organic solvents such as ethanol, ether, benzene, and chloroform, but is only slightly soluble in water. Any of these solvents could be used to trap nickel carbonyl. Impingers filled with any of these solvents would provide a satisfactory collection system for nickel carbonyl in dilute auto exhaust. A filter would be required to remove any particulate present in the exhaust prior to the impinger. The advantages are the simplicity of the procedure and the speed of determination. Experiments would have to be conducted to determine any possible interferences.

An alternative procedure would be to use nitric acid instead of hydrochloric or sulfuric acid in a colorimetry method. Nickel carbonyl reacts vigorously with nitric acid but reacts slowly with hydrochloric or sulfuric acid. Although this method is considered a good procedure, it is manpower intensive and requires much wet chemical work.

Metal carbonyls are used to make carboxylic acids.[295] Perhaps a technique could be developed to produce a derivative quantitatively. This would then allow an indirect method of determination. This method would require much development work to make it operative.

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XI. Sulfuric Acid

A. General Description(296,297)

Sulfuric acid is a colorless, oily liquid which has a freezing point of 10.5°C and a boiling point of 338°C. Sulfuric acid is also known as hydrogen sulfate and the chemical formula H_2SO_4. The molecular weight of H_2SO_4 is 98.08 and the density of the liquid at 20°C is 1.841 g/ml. The strong affinity of concentrated sulfuric acid for water makes it a good dehydrating agent. The amount of sulfuric acid used in industry exceeds that of any other manufactured compound.

B. Results of Literature Search

Upon initiating the literature search, it became apparent that a number of analytical techniques for measuring sulfuric acid have been applied to automotive exhaust. Since it was felt that a sufficient variety of procedures had been applied to measuring sulfuric acid in exhaust, the literature search was directed to reviewing those techniques.(298-326) Methods that have been applied to measuring sulfate in exhaust include barium perchlorate titration(323,324), barium chloranilate method(323,325), iodate titration(323), and microgravimetric analysis.(323)

The barium perchlorate titration is a general technique that has been applied to the analysis of samples obtained on filters, by controlled condensation or in isopropyl alcohol bubblers. Soluble sulfates collected on a filter are leached from the filter with nitric acid. This leach solution is heated to boiling to remove excess acid, filtered to remove insolubles and passed through an ion-exchange column to remove interfering cations. After buffering the solution with methenamine to a pH of 3-4, the resulting solution is titrated with barium perchlorate using Sulfonazo (III) as an indicator. Samples collected in a controlled condensation apparatus are removed by rinsing the coils and frit with deionized water. The resulting solution is boiled down to about 5 ml, buffered to a pH of 3-4 with methenamine and titrated in the same manner as samples from filter systems. One variation of this method is to extract filters in hot water, using thorin as an indicator.

If the sample was collected in isopropyl alcohol filled impingers, the absorbing solutions are evaporated to a low volume. The solution is then passed through an ion exchange resin to remove any cations that would interfere by reacting with the indicator. The purified solutions are titrated with standard barium perchlorate solution using thorin and methylene blue as an indicator.

The barium chloranilate (BCA) method involves the analysis of water soluble sulfate collected on Fluoropore filters during the emissions tests. The filter is ammoniated using NH_4OH, extracted in a 60% IPA solution, and analyzed in a specially designed high pressure liquid chromatograph system. This extract is injected into a high pressure liquid chromatograph by means of a liquid sampling valve. The extraction solvent and LC solvent are both 60% IPA. The extract passes through ion exchange resins to remove any interfering species and then through a column of barium chloranilate. The $BaSO_4$ precipitates out and an equivalent amount of violet colored chloranilic acid ion is released and quantitatively measured colorimetrically at 310 nm.

The iodate method is used to determine sulfate collected on glass fiber filters. The sulfate is leached from the filter with a warm aqueous solution containing $NaCO_3$ to eliminate lead ion interference. An aliquot of this solution is added to an ethanol solution containing formaldehyde to remove sulfite ion interference. Barium iodate is added, along with the starch indicator, and the characteristic starch-iodine color is measured spectrometrically at 590 nm.

Sulfate has also been measured microgravimetrically in solutions ranging from 1 to 100 mg. The solution is diluted to 100 ml, treated with HCl and heated to near boiling. Barium chloride is added gradually while stirring vigorously. The precipitate is allowed to nucleate on a steam bath overnight at 80°C. The precipitate (and solution) is transferred to a preweighed filter paper and washed with deionized water, ethyl alcohol and ethyl ether. The filter and precipitate are transferred to a drying oven and dried for one hour at 100°C. The filter and precipitate are cooled in a desiccator and weighed on a semimicrogram balance.

A substantial amount of data on sulfuric acid emissions has been published using these techniques. Of the aforementioned techniques, the BCA method is the most widely used. A number of cross checks between EPA, EPA contractors, and industry researchers have been conducted using a variety of sulfuric acid levels and included a variety of analytical procedures. The general concensus was that the BCA technique was more accurate at low sulfate levels that are anticipated in auto exhaust. Other techniques, such as the titration or microgravimetric, required substantially more sample than was required by the BCA method.

C. Recommendations

Based on the results of the literature search combined with practical experience of Southwest Research Institute and EPA, it is recommended to use the barium chloranilate method for measuring sulfuric acid in exhaust. This method has been developed by EPA as a method for measuring sulfate in automotive exhaust. Refinements to the original procedure are incorporated into the SwRI system and attempts will be made to keep abreast of any additional improvements.

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APPENDIX B

ALDEHYDE AND KETONE PROCEDURE

THE MEASUREMENT OF ALDEHYDES AND KETONES IN EXHAUST

The measurement of aldehydes (formaldehyde, acetaldehyde, isobutyraldehyde, crotonaldehyde, hexanaldehyde, and benzaldehyde) and ketones (acetone and methylethylketone) in exhaust is accomplished by bubbling the exhaust through glass impingers containing 2,4 dinitrophenylhydrazine (DNPH) in dilute hydrochloric acid. The exhaust sample is collected continuously during the test cycle. The aldehydes and ketones (also known as carbonyl compounds) react with the DNPH to form their respective phenylhydrazone derivatives. These derivatives are insoluble or only slightly soluble in the DNPH/HCl solution and are removed by filtration followed by pentane extractions. The filtered percipitate and the pentane extracts are combined and then the pentane is evaporated in a vacuum oven. The remaining dried extract contains the phenylhydrazone derivatives. The extract is dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. A portion of this dissolved extract is injected into a gas chromatograph and analyzed using a flame ionization detector. The detection limits for this procedure under normal operating conditions are on the order of 0.005 ppm carbonyl compound in dilute exhaust.

LIST OF EQUIPMENT

The equipment required for the analysis of aldehydes and ketones is divided into three groups: sample acquisition, sample preparation, and sample analysis. Manufacturer, stock number and any pertinent descriptive information are listed.

Sample Acquisition

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.

2. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/min range.

3. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 ℓ/min.

4. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.

5. Regulating valve, Nupro 4MG, stainless steel.

6. Teflon tubing, United States Plastic Corporation, 1/4" OD × 1/8" ID and 5/16" OD × 1/8" ID.

7. Teflon solenoid valve, The Fluorocarbon Company, Model DV2-144NCA1.
8. Drying tube, Analabs, Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.
9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.
10. Digital readout for dry gas meter.
11. Miscellaneous electrical switches, lights, wirings, etc.
12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.
13. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.
14. Variable autotransformer, Staco Inc., Type 3PN 1010.
15. Heating sleeve wrapped with insulation and insulation tape.
16. Class A, 20 mℓ volumetric pipets.
17. Class A, 1000 mℓ volumetric flask.
18. Teflon coated stirring bar.
19. Hot plate-stirrer, Corning, PC-351.

Sample Analysis

1. Varian 1700 gas chromatograph equipped with dual flame ionization detectors in differential operation, and a linear temperature programmer.
2. Soltec Model B-281 1 mv recorder.
3. Hewlett-Packard Model 3354 gas chromatograph computer system with remote teletype printout.
4. Syringe, 10 mℓ, Hamilton Company, #701.
5. Dual columns, 24 × 1/8" OD, stainless tubing packed with 6.7 percent Dexsil 300 GC on Chromosorb G 60/80 mesh, DMCS treated and acid washed.

Sample Preparation

1. Fritted glass filters, Ace Glass Company, porosity D, ASTM 10 - 20 microns pore size, 24/40 ground glass joint, vacuum takeoff.

2. Constant temperature vacuum oven, National Appliance Company.
3. Pump for oven, Thomas Industries, Model 907CA18 2.
4. Flasks, 125 mℓ capacity, 24/40 ground glass joints.
5. Separatory funnels, 125 mℓ.
6. Separatory funnels, 250 mℓ.
7. Separatory funnel shaker, Burrell Corporation, Wrist-Action® type with appropriate funnel holders, Model 75.
8. Ring stands, labels, holders, tubing, vacuum tubing, fittings and clamps needed for equipment manipulation.
9. Wash bottles, 500 mℓ.
10. Graduated cylinders, 50 mℓ.
11. Vials, Kimble, 1/2 dram.
12. Vacuum pump, Sargent-Welch.

LIST OF REAGENTS

A list of the reagents used in the determination of the aldehydes and ketones in exhaust is provided along with chemical formula, molecular weight, purity, manufacturer, and catalog number.

1. Hydrochloric acid, HCl, 36.46 g/mole, concentrated (37%), analytical reagent, Mallinckrodt, Cat. #2612.
2. Pentane, C_5H_{12}, 72.15 g/mole, Distilled in glass (bp 35-37°C), Burdick and Jackson Laboratories, Inc.
3. 2,4 Dinithrophenylhydrazine (2,4-DNPH), $(NO_2)_2C_6H_3CH{=}N-NH_2$, 210.149 g/mole, Aldrich analyzed, Aldrich, Cat. #D19,930-3.
4. Sodium Bicarbonate, $NaHCO_3$, 84.00 g/mole, Mallinckrodt, Cat. #7412.
5. Anthracene, $C_{14}H_{10}$, 178.24 g/mole, K and K Laboratories, Cat. #10714.
6. Toluene, $C_6H_5CH_3$, 92.14 g/mole Baker Analyzed Reagent, Baker Cat. #3-9460.
7. Methylene Chloride, CH_2Cl_2, 84.93 g/mole, Reagent ACS, Eastman, Cat. #13022.

PREPARATION OF ABSORBING SOLUTION

To prepare the absorbing solution, 163 mℓ of concentrated HCl and 2.5 g of 2,4-DNPH crystals are added to a one liter volumetric flask containing about 500 mℓ of deionized water. The flask is diluted to mark and stirred for several hours at room temperature with an automatic stirrer/teflon coated stirring bar to dissolve the DNPH. Fresh absorbing solution is prepared daily as needed.

PREPARATION OF TOLUENE/ANTRACENE SOLUTION

Toluene containing approximately 0.05 mg anthracene per mℓ of toluene is used to dissolve the dried phenylhydrazone extracts. This solution is made by adding 100 mg of anthracene to a two liter volumetric flask and diluting to mark with toluene.

PREPARATION OF PHENYLHYDRAZONE DERIVATIVES

In order to obtain response factors for each of the phenylhydrazone derivatives to anthracene, pure derivatives were prepared from their respective aldehydes and ketones. These derivatives were made by adding each of the carbonyl compounds separately to a 2N HCl-DNPH solution. The resulting orange to red precipitates were filtered and dried. The derivatives were then recrystallized from hot absolute ethanal. The melting points for each of the derivatives were compared to literature values before use. A GC trace was also made on each of the derivatives to further check the purity.

PREPARATION OF STANDARD SOLUTION OF PHENYLHYDRAZONE DERIVATIVES AND ANTRACENE

A standard containing the phenylhydrazone derivatives and anthracene in toluene is prepared to obtain a response factor of each of the derivatives to anthracene. The solution is made by dissolving weighed amounts of anthracene and each of the derivatives in a quantitative volume of toluene. These solutions contain approximately 0.05 mg anthrancene per mℓ of toluene and approximately 0.2 mg of each derivative per mℓ of toluene.

SAMPLING SYSTEM

Two glass impingers in series, each containing 40 mℓ of 2N HCl-2,4 dinitrophenylhydrazine, are used to collect exhaust samples for the analysis of the aldehydes and ketones. A flow schematic of the sample collection system is shown in Figure 1. The two impingers together trap approximately 98 percent of the carbonyl compounds. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. The dry gas meter determines the total flow through the impinger during a given driving cycle. The sample pump is capable of pulling a flow rate of 4 ℓ/min. A drier is included to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter allows continuous monitoring of the sample flow to insure proper flow rates during the sampling. The Teflon line connecting the CVS and the solenoid valve is heated to ∿170°F in order to prevent water from condensing in the line. Several views of the sampling system are shown in Figure 2.

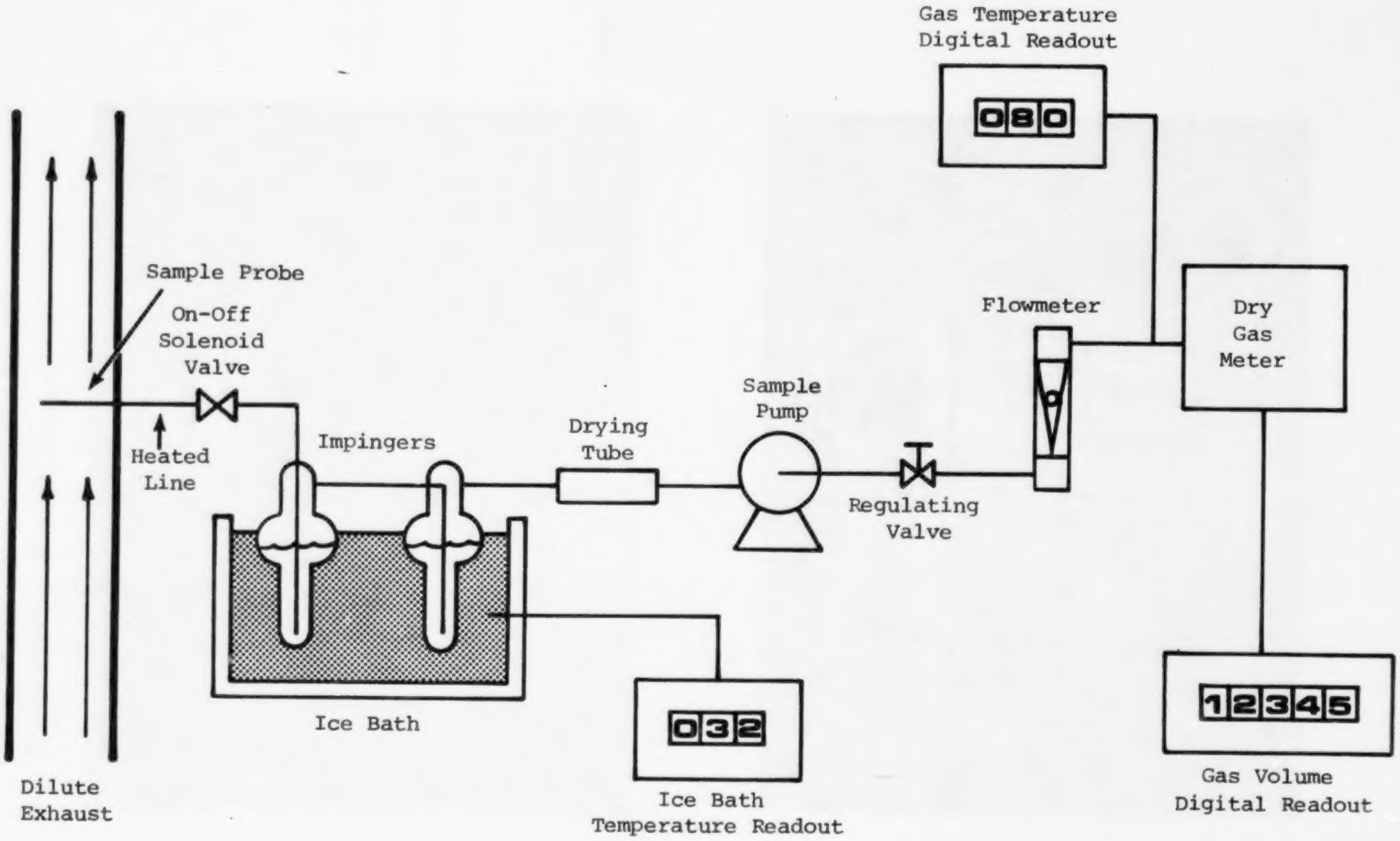
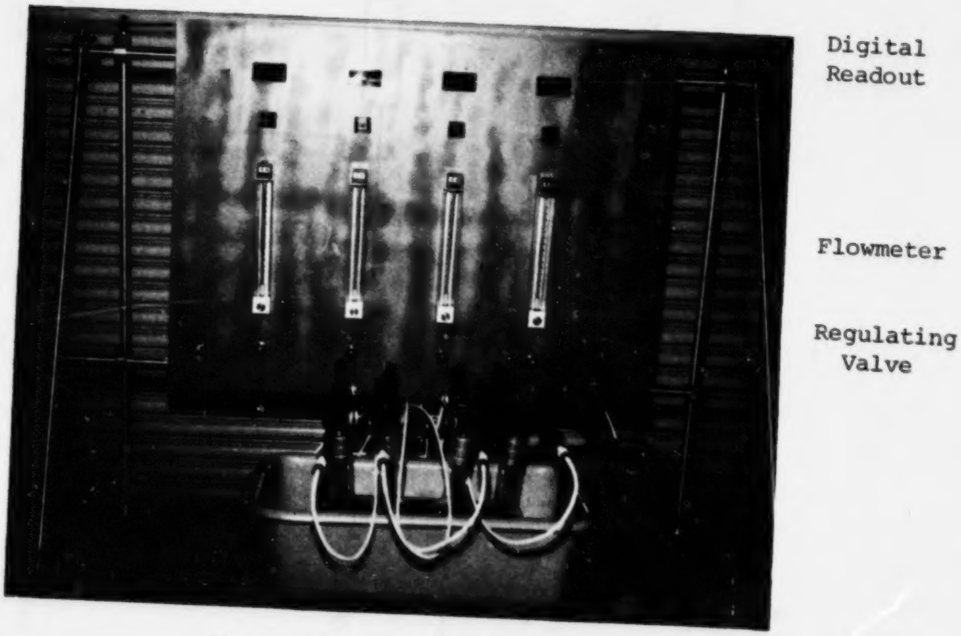

Gas Temperature
Digital Readout
080
Sample Probe
On-Off
Solenoid
Valve
Flowmeter
Dry
Gas
Meter
Sample
Pump
Impingers
Drying
Tube
Heated
Line
Regulating
Valve
Ice Bath
032
12345
Dilute
Exhaust
Ice Bath
Temperature Readout
Gas Volume
Digital Readout

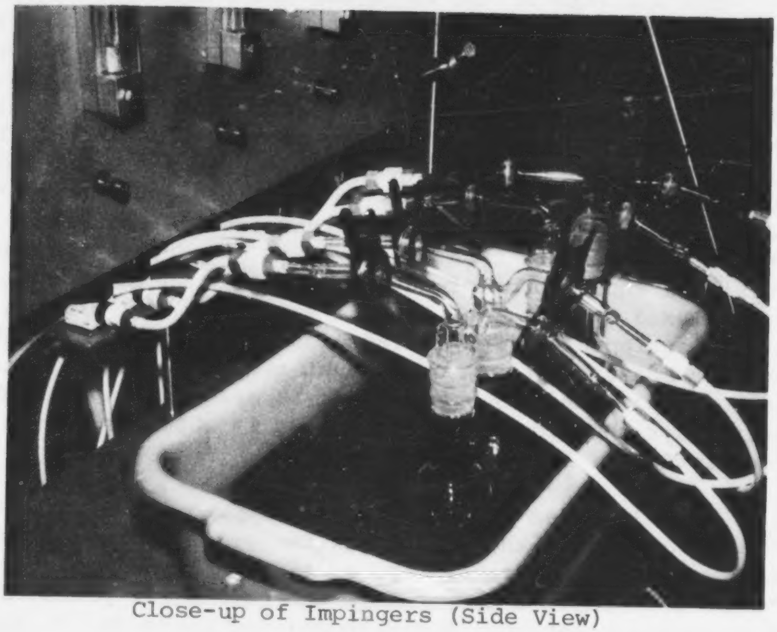
Figure 1. Aldehyde and Ketone sample collection flow schematic.

Front View


Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. Aldehyde and Ketone sampling system.

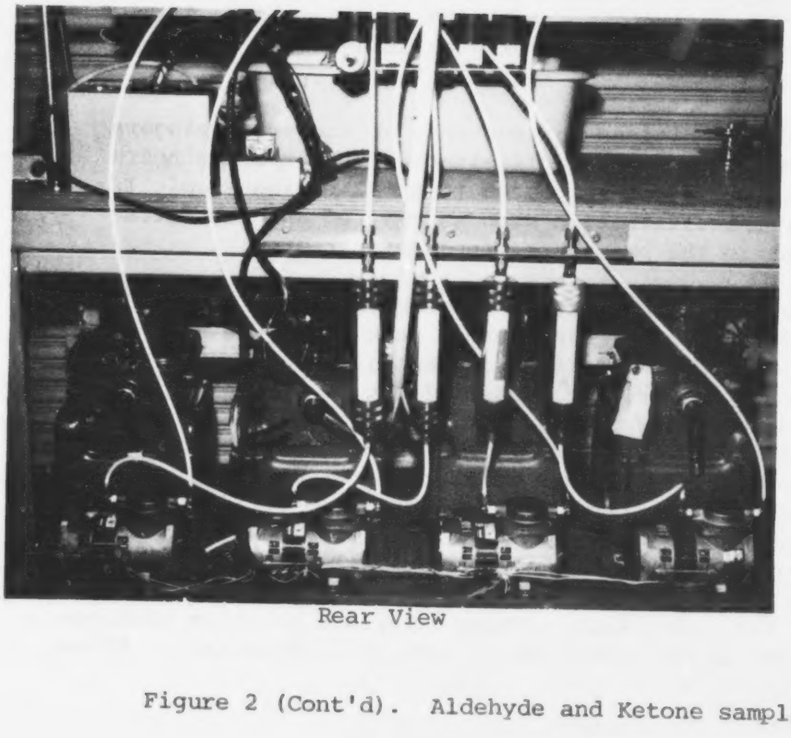


Solenoid

Impinger

Ice Bath

Close-up of Impingers (Side View)



Solenoid
Filter

Ice Bath

Drier

Dry Gas Meter

Pump

Rear View

Figure 2 (Cont'd). Aldehyde and Ketone sampling system.

ANALYTICAL PROCEDURE

The analysis of the aldehydes (formaldehyde, acetaldehyde, isobutyraldehyde, crotonaldehyde, hexanaldehyde, and benzaldehyde) and of the ketones (acetone and methylethylketone) in dilute exhaust is accomplished by collecting these carbonyl compounds in a hydrochloric acid (HCl)/2,4 dinitrophenylhydrazine (DNPH) solution as their 2,4 dinitrophenylhydrazone derivatives. The derivatives are removed from the HCl/DNPH absorbing solution by filtration and/or extractions with pentane. The filtered preciptate and the pentane extracts are combined and the volatile solvents are removed. The remaining extract contains the phenylhydrazone derivatives. The derivatives are then dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. This solution is analyzed by injecting a small volume of the solution into a gas chromatograph equipped with dual flame ionization detectors. From this analysis and the measured volume of exhaust sampled, the concentration of the carbonyl compounds in exhaust can be determined. The analysis flow schematic for the aldehydes and ketones is shown in Figure 3. A detailed description of the procedure follows.

The aldehydes and ketones are trapped in solution by bubbling a known volume of dilute exhaust through two glass impingers connected in series, with each impinger containing 40 mℓ of a 2N HCl solution saturated with DNPH. The sampling temperature and barometric pressure are recorded during this bubbling period. The carbonyl compounds in the exhaust react with the DNPH to form slightly soluble or insoluble 2,4 dinitrophenylhydrazone derivatives. The two impingers together collect 98 percent + of the carbonyls that are present in the exhaust. The impingers are removed from the sampling cart and are allowed to stand at room temperature for at least one hour before proceeding to the filtration and extraction steps. Figure 4 shows two impingers containing the HCl/DNPH absorbing solution after being removed from the sampling cart.

Under normal operating conditions the contents of the two impingers are combined and analyzed as one sample. If either of the two impingers contain a precipitate they are first subjected to a filtration step. If no percipitate is present this filtration step is omitted and the extraction step, described later in the procedure, is the first step.

For the filtration step the contents of the two impingers are poured through a fritted glass filter into a flask under vacuum (Figure 5). The two impingers are rinsed with small portions of deionized water. This wash water is also poured through the fritted glass filter. The precipitate in the filter is then washed with a few mℓ of deionized water. The fritted filter is then removed from the flask containing the 80 mℓ of absorbing reagent and the water washings. The flask is then set aside for the extraction step. The fritted glass filter containing the precipitate is connected to a dry flask. The two impingers that had previously contained the filtered precipitate are then each washed with small portions of methylene chloride. The methylene chloride dissolves any solid residue which was not removed by the water wash. These methylene chloride washings are poured into the fritted glass filter containing the precipitate. After

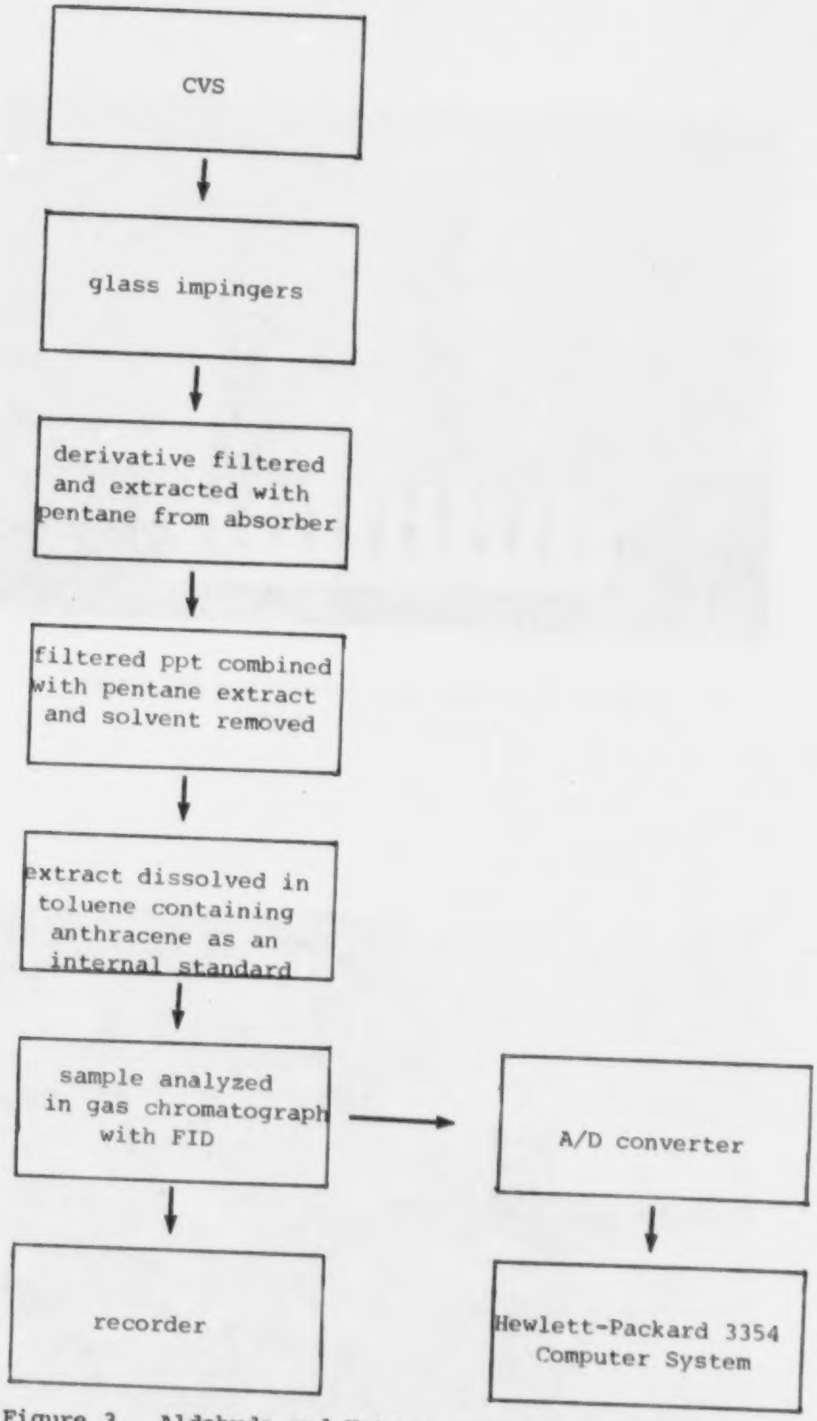

CVS
glass impingers
derivative filtered and extracted with pentane from absorber
filtered ppt combined with pentane extract and solvent removed
extract dissolved in toluene containing anthracene as an internal standard
sample analyzed in gas chromatograph with FID
A/D converter
recorder
Hewlett-Packard 3354 Computer System

Figure 3. Aldehyde and Ketone analysis flow schematic.

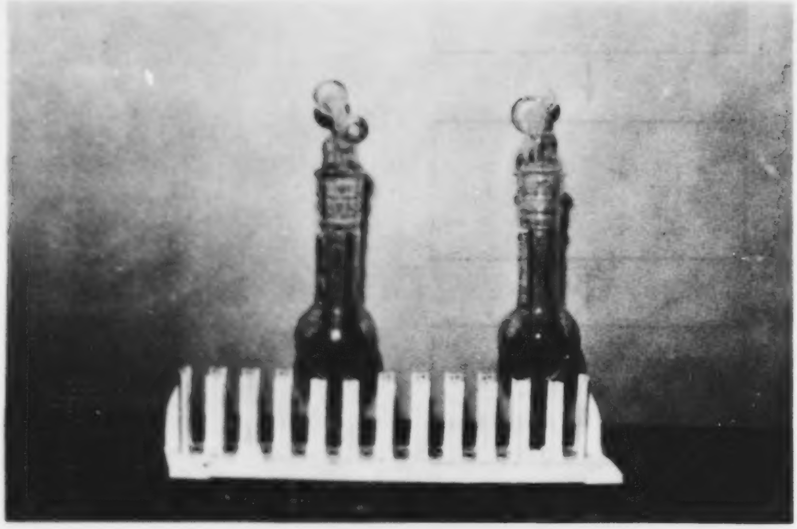


Figure 4. Impingers containing HCl/DNPH absorbing solution.

Figure 5. Filtration of absorbing solution.

the precipitate has been dissolved by the methylene chloride, a vacuum is applied to the flask and the methylene chloride solution is pulled through the filter into the flask. Another small amount of methylene chloride is poured through the filter into the flask to wash the filter. The methylene chloride solution is now saved until the extraction step is complete.

The extraction step is carried out as follows. The contents of the two impingers (if no precipitate is present) are transferred to a 250 mℓ separatory funnel. The impingers are each washed with small portions of deionized water which is also added to the separatory funnel. If a precipitate was found in the impingers the contents of the flask containing the filtered absorbing reagent and the water washings from the filtration step are transferred quantitatively to a 250 mℓ separatory funnel. The flask is washed with a small portion of water, and this water is added to the separatory funnel. Forty mℓ of pentane is now added to the separatory funnel containing the 80 mℓ of absorbing reagent and water washings. The funnel is stoppered and shaken for five minutes in an automatic shaker, Figure 6. The shaker is stopped and the funnel is vented. After the two phases are allowed to separate, the lower phase is collected in a second separatory funnel. The remaining phase is transferred to a third 250 mℓ separatory funnel. A second 40 mℓ portion of pentane is added to the already once extracted absorbing solution. The funnel is again stoppered, shaken for 5 minutes and vented. After the phases have separated the lower phase is again collected in another separatory funnel. The upper or pentane layer is combined with the pentane layer from the first extraction. A third 40 mℓ portion of pentane is added to the twice extracted absorbing solution and the extraction process repeated. After the third extraction the lower layer is discarded and the pentane layer is combined with the pentane layers from the first two extractions. Any absorbing solution which might have been accidently transferred with the pentane layers is drained off. Deionized water (25-50 mℓ) and sodium bicarbonate (1/4-1/2 gram) is added to the 250 mℓ separatory funnel containing the 120 mℓ of pentane extract. The funnel is stoppered and manually shaken for 30 seconds. The phases are allowed to separate and the lower water phase is drained off. Another 25 mℓ of deionized water is added and the shaking is repeated. After the phases have separated, the water is drained off insuring that all traces of water are removed. The contents of the funnel are then combined with the methylene chloride solution which was saved from the filtration step.

The flask containing the methylene chloride solution and the pentane extracts is then placed in a vacuum oven, Figure 7, operating at 50-60°C and 65" water vacuum until the pentane and methylene chloride have been removed. At this time only the dried phenylhydrazone derivatives remain.

Each time a series of samples are collected a blank containing 80 mℓ of HCl/DNPH solution is extracted and dried in the same manner as the samples. This accounts for any aldehydes or interfering compounds which might be found in the reagents used for extraction.

Two mℓ of toluene which contain a quantitative amount of anthracene (∿0.05 mg/mℓ toluene) as an internal standard is pipetted into the flask

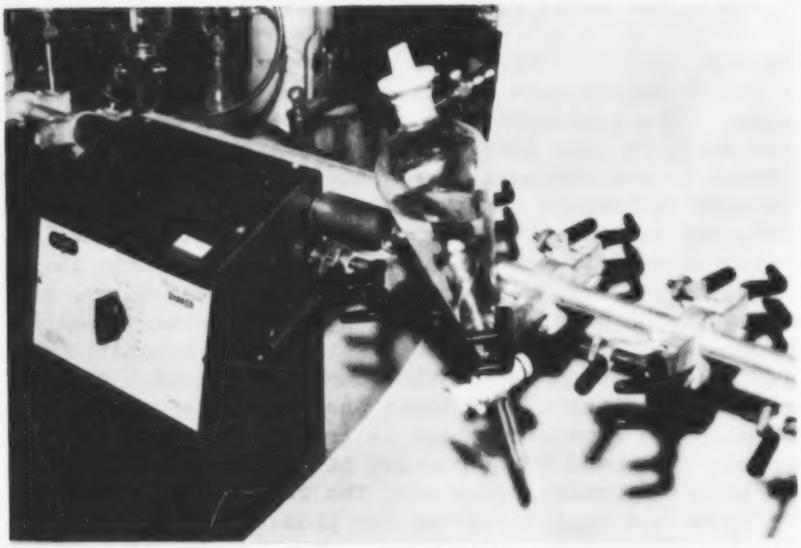


Figure 6. Automatic shaker.

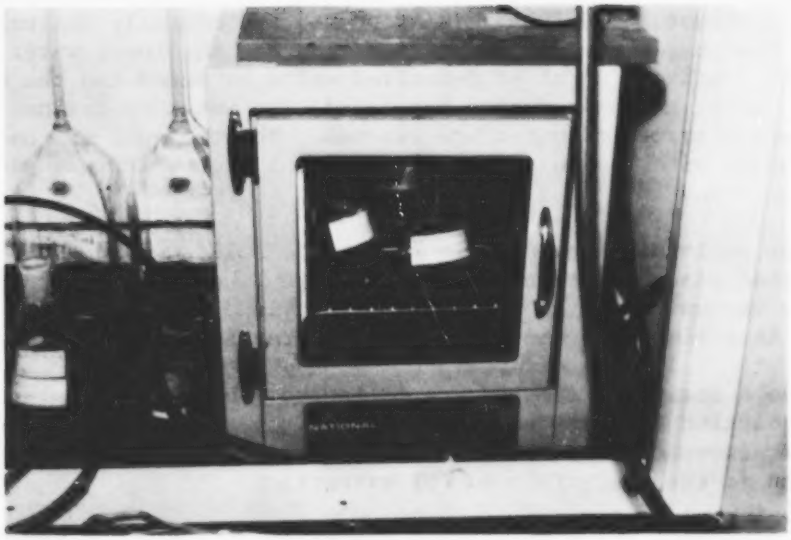


Figure 7. Vacuum oven.

containing the dried phenylhydrazone derivatives. The flask is then placed in a sonic bath until all of the residue is dissolved. After the precipitate has dissolved, the solution is transferred to a 1/2 dram vial. (See Figure 8.) At this point the derivative is ready for injection into the gas chromatograph system.

The gas chromatograph system used to analyze the toluene solution containing the phenylhydrazone derivatives is shown in Figure 9. The system consists of a Varian 1700 GC, an A/D converter, and a recorder. The GC is equipped with dual columns and dual flame ionization detectors with a single differential amplifier. The columns consist of 24 × 1/8 inch O.D. stainless steel tubing packed with 6.7 percent Dexsil (polycarboranesiloxane) 300 GC on DMCS treated and acid washed, 60/80 mesh Chromosorb G. The carrier gas is helium which flows through the columns at a rate of 40 mℓ/min. The optimum hydrogen and air flow rates are 500 mℓ/min and 35 mℓ/min respectively. The column temperature, after injection of the sample, is programmed from 120°C to 300°C at 8° a minute. In a chromatogram of a standard sample (Figure 10) containing anthracene and the phenylhydrazone derivatives of formaldehyde, acetaldehyde, acetone, iso-butyraldehyde, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde, the first peak eluted is toluene followed by anthracene, and then the derivatives of formaldehyde, acetaldehyde, acetone, iso-butyraldehyde, methylethylketone, crotonaldehyde, hexanaldehyde and benyaldehyde. The methylethylketone derivative is added to the list of derivatives in order to name an unknown peak found in some of the exhaust samples. Data obtained from the five repetitive injections of the standard derivatives in toluene showed a maximum standard deviation of 4.56 percent for benzaldehyde and a minimum standard deviation of 0.87 percent for formaldehyde. The computer printout of the standard, Figure 10, is shown in Figure 11. This printout gives the retention time, area, and the name of each peak. The printout also gives the concentration of each of the derivatives in mg/mℓ. This concentration is calculated by the computer from response factors which are determined daily. Each day a standard containing known amounts of the derivatives and anthracene is injected into the GC. From the anthracene and derivative areas the computer calculates a response factor F. These F factors are used in all subsequent runs during the day to determine the concentration of the derivatives. This response is calculated from the following equation:

$$\text{Response Factor (F)} = \frac{\text{Anthracene Area}}{\text{Derivative Area}} \times \frac{\text{mg/m}\ell\text{ Derivative}}{\text{mg/m}\ell\text{ Anthracene}}$$

Typical response factors for each of the derivatives are listed below:

FACTOR	NAME
1.0000	ANTHRACENE
3.1043	FORMALDEHYDE
2.7736	ACETALDEHYDE
2.2366	ACETONE
2.4160	ISO-BUTYRALDEHYDE
2.3332	METHYLETHYLKETONE
3.4174	CROTONALDEHYDE

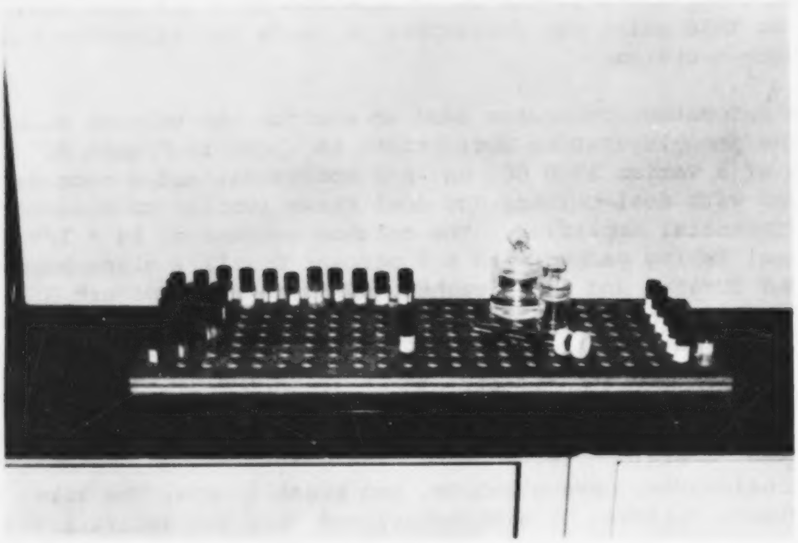


Figure 8. 1/2 dram vials.

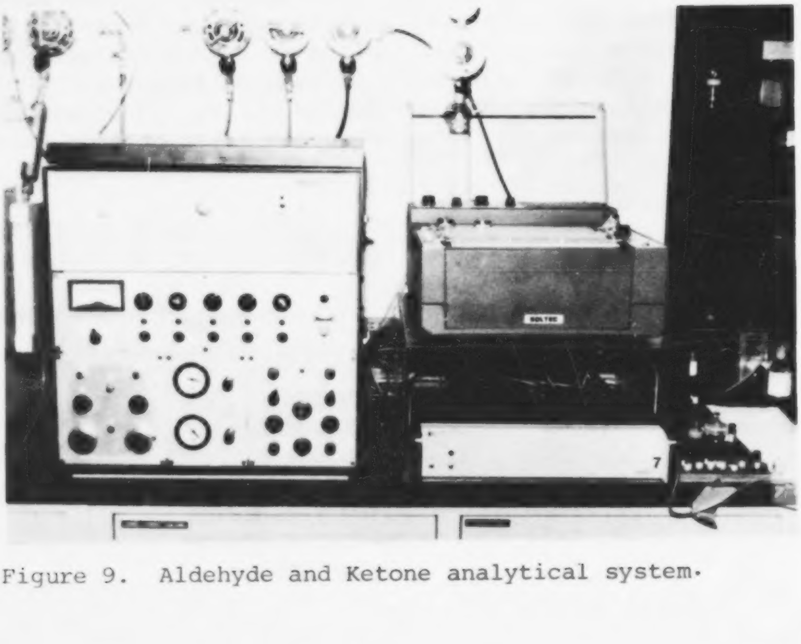


Figure 9. Aldehyde and Ketone analytical system.

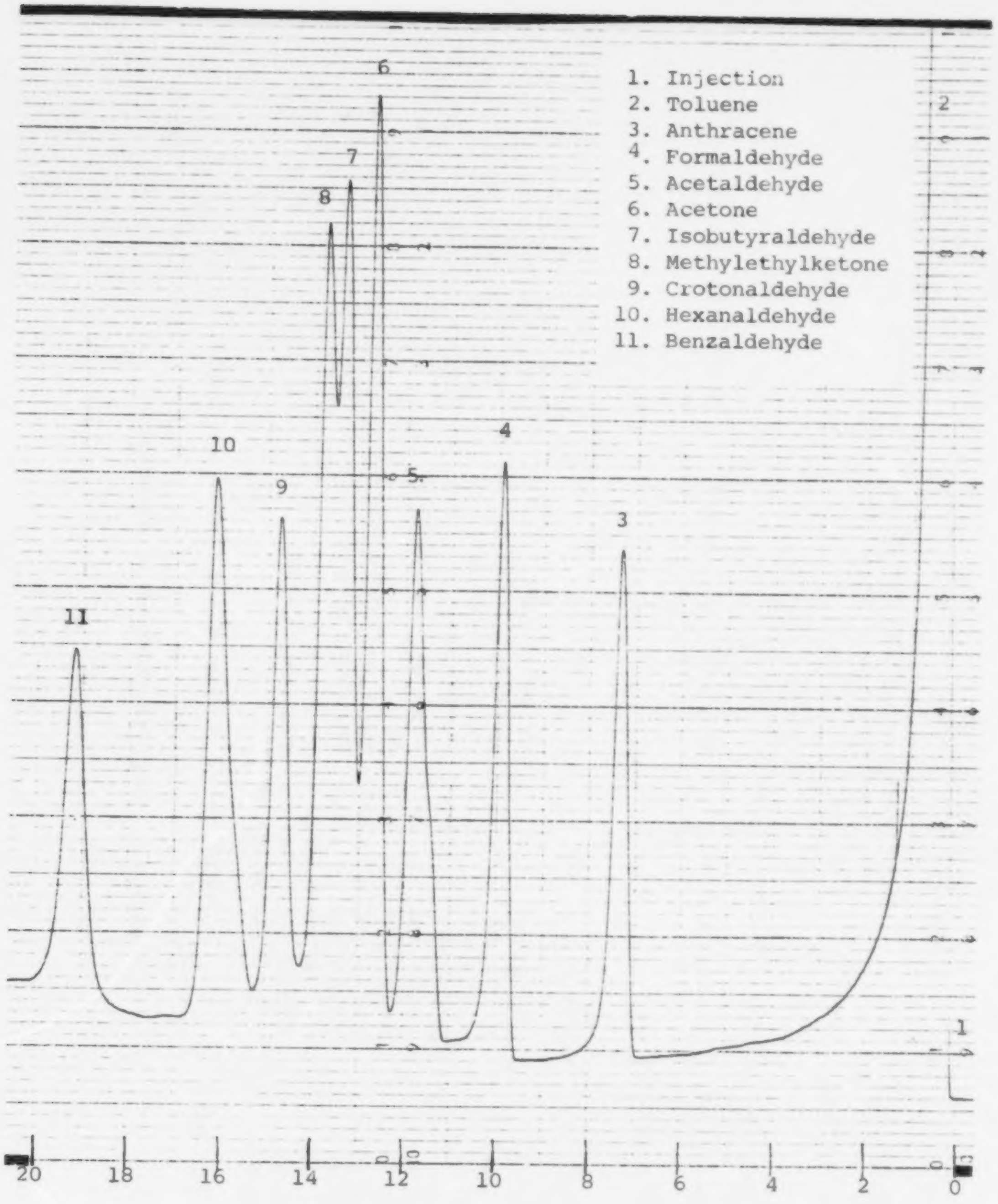


Figure 10. Chromatogram of standard.

```
REPORT:    14.11  CHANNEL: 11

SAMPLE: RCI           INJECTED AT  11:18:27 ON MAR  1, 1978

ISTD METHOD: DNPH11


ACTUAL RUN TIME:  30.008 MINUTES

ISTD-RATIO:    .050,R MG/ML    STD-AMT:      .0500    SAMP-AMT:    1.0000

ENDED NOT ON BL


   RT        AREA        MG/ML         NAME

  7.26        9638 BB              &ANTHRACENE
  9.81       11159 BB     .190   #FORMALDEHYDE
 11.71       13355 BV     .202   #ACETALDEHYDE
 12.64       17898 VV     .211   #ACETONE
 13.28       16448 VV     .210   #ISO-BUTYRALDEHYDE
 13.70       16469 VV     .207   #MEK
 14.69       11167 VV     .208   #CROTONALDEHYDE
 16.08       15988 VV     .206   #HEXANALDEHYDE
 17.08          74 VB 3.8E- 4
 19.08       10525 BB     .215   #BENZALDEHYDE
 25.04         187 BB 9.7E- 4

TOTAL AREA =       122909       TOTAL MG/ML  =      1.650
```

Figure 11. Computer printout of standard.

2.3428	HEXANALDEHYDE
2.9329	BENZALDEHYDE

When the response factor is known a concentration in mg/mℓ for each of the derivatives can be found. This concentration, along with the volume of sampled exhaust is then used to calculate the concentration of the carbonyl compounds in exhaust. Figures 12 and 13 show a typical sample chromatogram and accompanying printout respectively.

CALCULATIONS

This procedure has been developed to provide the user with the concentrations of the aldehydes (formaldehyde, acetaldehyde, isobutyraldehyde, crotonaldehyde, hexanaldehyde, and benzaldehyde) and ketones (acetone and methylethylketone) in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm for each carbonyl compound. The equations for determing the concentrations in $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F and pressure, 29.92" Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92" Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92" Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R)\quad 29.92\text{" Hg}}$$

The next step converts the volume from cubic feet to cubic meters by use of the conversion factor 1 cubic meter is equal to 35.31 cubic feet.

$$V_{corr(m^3)} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°}{T_{exp} \times 29.92\text{" Hg} \times 35.31\ ft^3/m^3}$$

(Equation 1)

The next step converts the mg/mℓ of derivative determined by the computer to mg of carbonyl collected in the two impingers. To obtain mg of derivative, the concentration (from the computer printout) in mg/mℓ is multiplied by the volume of toluene used to dissolve the solid extract.

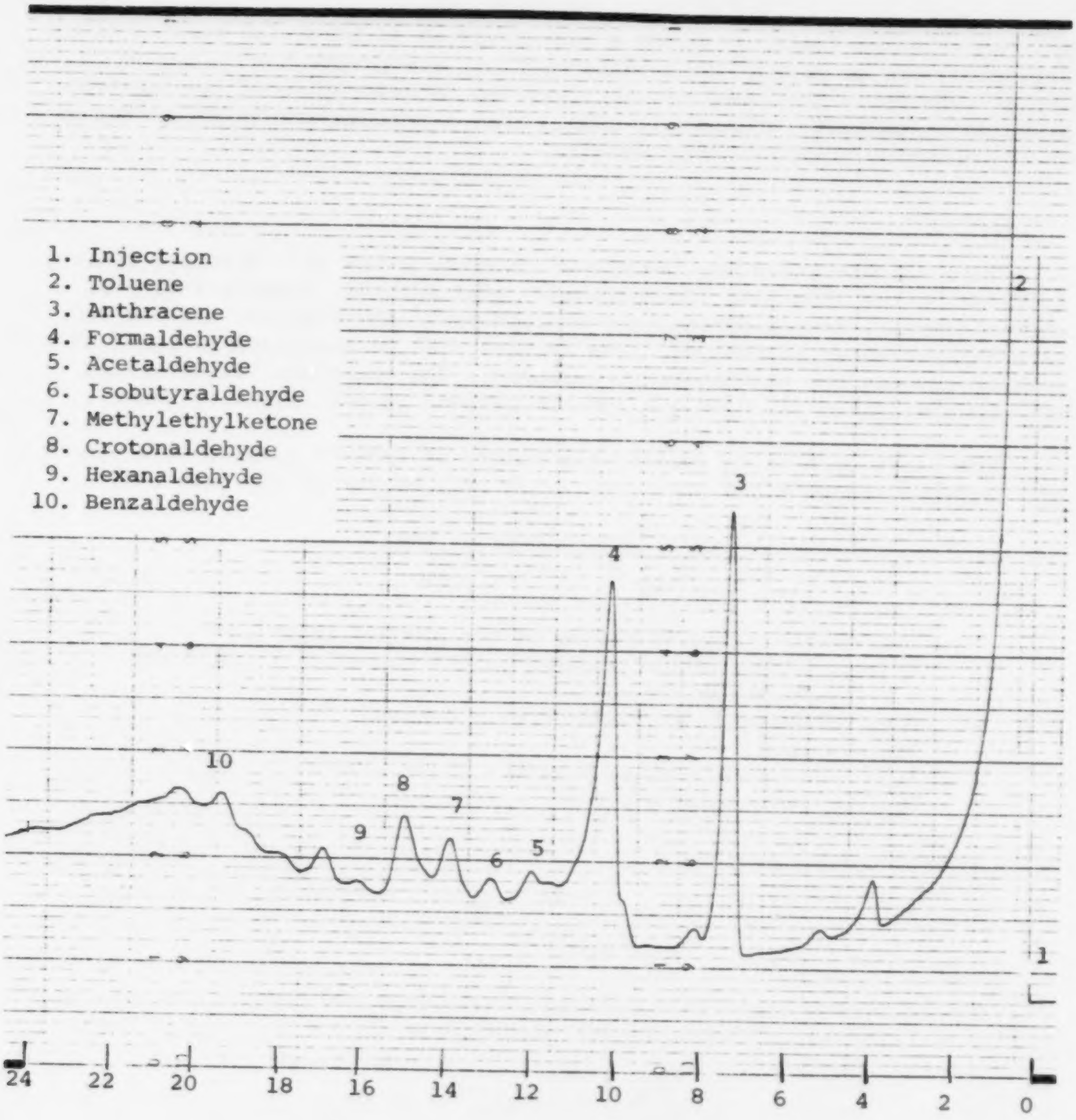
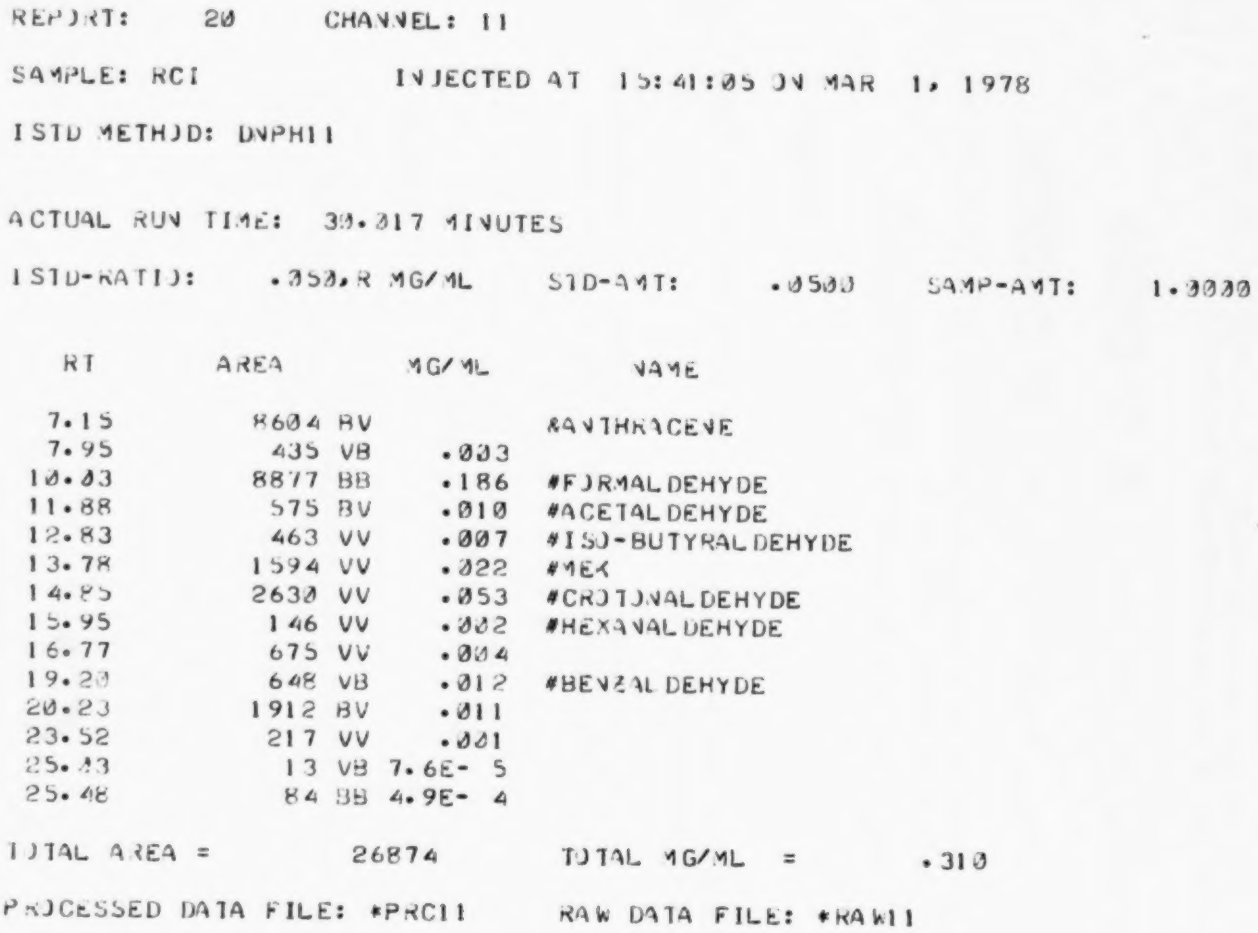


Figure 12. Sample chromatogram.



```
REPORT:     20      CHANNEL: 11

SAMPLE: RCI              INJECTED AT  15:41:05 ON MAR  1, 1978

ISTD METHOD: DNPH11


ACTUAL RUN TIME:  30.017 MINUTES

ISTD-RATIO:     .050,R MG/ML     STD-AMT:      .0500    SAMP-AMT:    1.0000

    RT        AREA        MG/ML         NAME

    7.15        8604 BV             &ANTHRACENE
    7.95         435 VB      .003
   10.03        8877 BB      .186   #FORMALDEHYDE
   11.88         575 BV      .010   #ACETALDEHYDE
   12.83         463 VV      .007   #ISO-BUTYRALDEHYDE
   13.78        1594 VV      .022   #MEK
   14.85        2630 VV      .053   #CROTONALDEHYDE
   15.95         146 VV      .002   #HEXANALDEHYDE
   16.77         675 VV      .004
   19.20         648 VB      .012   #BENZALDEHYDE
   20.23        1912 BV      .011
   23.52         217 VV      .001
   25.43          13 VB 7.6E- 5
   25.48          84 BB 4.9E- 4

TOTAL AREA =         26874      TOTAL MG/ML   =       .310

PROCESSED DATA FILE: *PRC11     RAW DATA FILE: *RAW11
```

Figure 13. Computer printout of sample.

$$\text{mg derivative} = \text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell)$$

To find mg of carbonyl compound per sample the mg of derivative are multiplied by the ratio of the molecular weight of the carbonyl derivative over the molecular weight of its phenylhydrazone derivative.

$$\text{mg carbonyl} = \text{mg derivative} \times \frac{\text{mol. wt. carbonyl}}{\text{mol. wt. derivative}}$$

$$= \text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \frac{\text{mol. wt. carbonyl}}{\text{mol. wt. derivative}}$$

To obtain the number of μg of carbonyl compound the mg of carbonyl are multiplied by the conversion factor, 1000 μg/mg

$$\mu\text{g carbonyl} = \text{Conc}_{\text{Der}}\ (\text{mg/m}\ell)\ \text{x}\ \text{Vol}_{\text{Tol}}(\text{m}\ell)\ \text{x}\ \frac{\text{Mol. Wt. carbonyl}}{\text{Mol. Wt. derivative}}$$
$$\text{x}\ 1000\ \mu\text{g/mg}$$

(Equation 2)

The concentration of the carbonyl compound in exhaust can now be found in $\mu g/m^3$ by dividing equation 2 by equation 1.

$$\mu\text{g carbonyl/m}^3 = \frac{\text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \text{mol. wt. carbonyl}}{P_{\text{exp}}\ (\text{"Hg}) \times V_{\text{exp}}\ (\text{ft}^3) \times 528^\circ}$$

$$\times \frac{1000\ \mu\text{g/mg} \times T_{\text{exp}}\ (^\circ\text{R}) \times 29.29\text{" Hg} \times 35.31\ \text{ft}^3/\text{m}^3}{\text{mol. wt. derivative}}$$

(Equation 3)

To find the concentration of each carbonyl compound in ppm, the densities of carbonyls are needed. At 29.92" Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation.

$$\frac{V}{T} = \frac{V_1}{T_1}$$

V_1 = 22.4
T_1 = 32°F +460 = 492°R
V = volume at 68°F
T = 68°F + 460 = 528°R

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04ℓ at 68°F, the denisty can be found in g/ℓ by dividing the molecular weight in g/mole by 24.04 ℓ/mole

$$\text{den } (\text{g}/\ell) = \frac{\text{mol. wt. (g/mole)}}{24.04\ell/\text{mole}}$$

The density in μg/mℓ can be found by converting g to μg and μg and ℓ to mℓ as follows:

$$\text{den } \mu\text{g/m}\ell = \frac{\text{mol. wt. g/mole}}{24.04\ell/\text{mole}} \times \frac{1 \times 10^6 \ \mu\text{g/g}}{1 \times 10^3 \ \text{m}\ell/\ell} \times \frac{\text{mol. wt.} \times 1000}{24.04}$$

(Equation 4)

To obtain the concentration of each carbonyl in ppm, the concentration in μg/m³ is divided by the density in μg/mℓ

$$\text{ppm} = \mu\text{g/m}^3 \div \mu\text{g/m}\ell = \frac{\text{m}\ell}{\text{m}^3}$$

Using Equations 3 and 4 gives the ppm concentration in the form of the raw data.

$$\text{ppm} = \frac{\text{Conc}_{\text{Der}} \ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}} \ (\text{m}\ell) \times \text{mol. wt. carbonyl} \times 1000 \ \mu\text{g/m}\ell}{P_{\text{exp}} \ (\text{"Hg}) \times V_{\text{exp}} \ (\text{ft}^3) \times 528° \times \text{mol. wt. derivative}}$$

$$\times \frac{T_{\text{exp}} \ (°\text{R}) \times 29.92\text{" Hg} \times 35.31 \ \text{ft}^3/\text{m}^3 \times 24.04 \ \ell/\text{mole}}{\text{mol. wt. carbonyl} \times 1000}$$

$$= \frac{\text{Con}_{\text{Der}} \ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}} \ (\text{m}\ell) \times T_{\text{exp}} \ (°\text{R}) \times 29.92\text{" Hg}}{P_{\text{exp}} \ (\text{"Hg}) \times V_{\text{exp}} \ (\text{ft}^3) \times 528°}$$

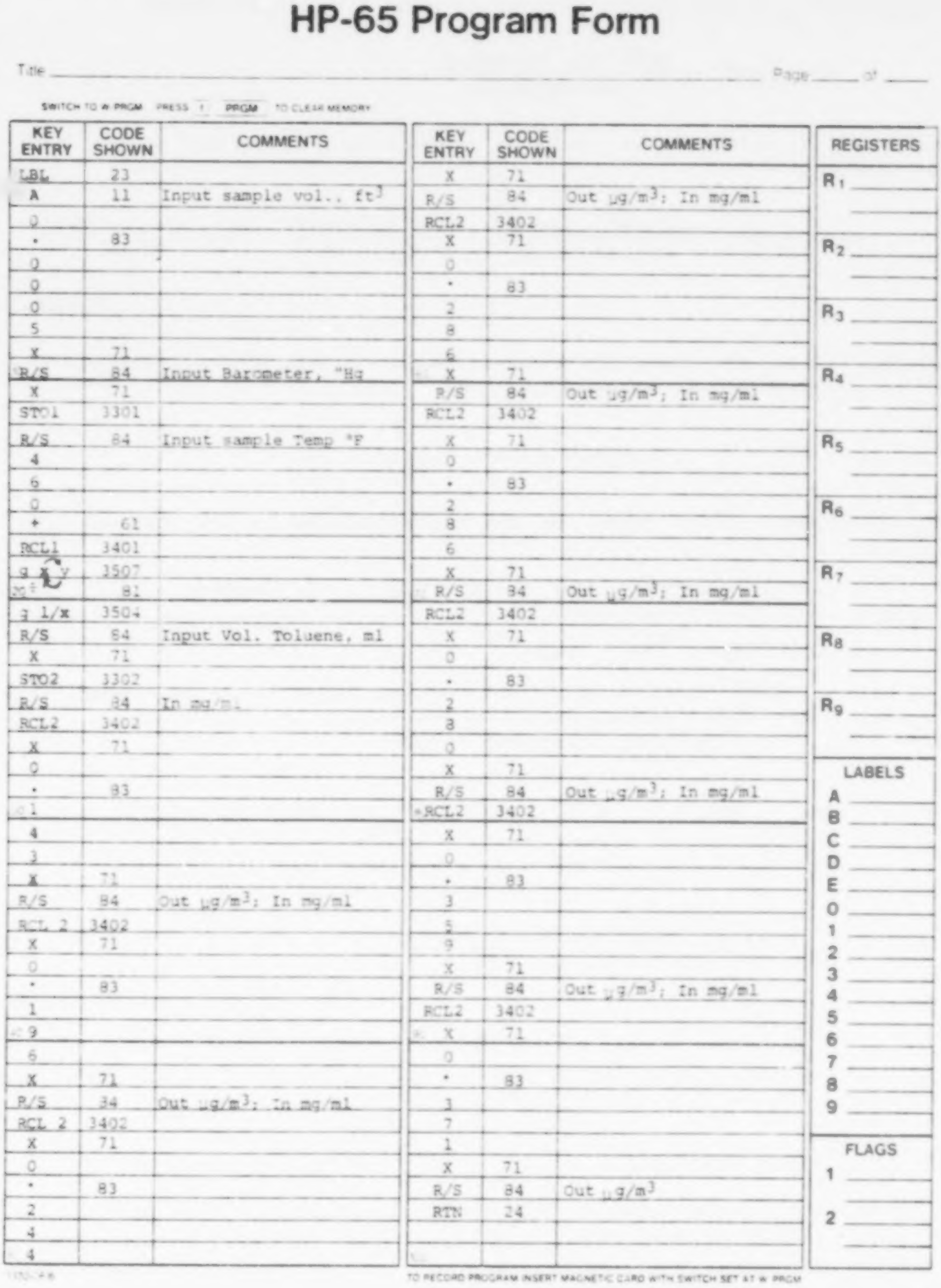
$$\times \frac{35.35 \ \text{ft}^3/\text{m}^3 \times 24.04 \ \ell/\text{mole}}{\text{mol. wt. derivative}}$$

(Equation 5)

At this point, the concentration can be express in μg/m³ (Equation 3) and ppm (Equation 5) at 68°F and 29.92" Hg from the raw data.

Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period, two Hewlett-Packard 65 programs were developed. One calculates the aldehyde and ketone concentrations in μg/m³ from the raw data and phenylhydrazone derivative concentrations (from computer printout). The other program calculates the concentrations in ppm from the concentrations in μg/m³. These programs are presented in Figures 14 and 15.



HP-65 Program Form

Title ______________________________ Page ____ of ____

SWITCH TO W/PRGM PRESS f PRGM TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS	KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23		X	71	
A	11	Input sample vol., ft^3	R/S	84	Out µg/m^3; In mg/ml
0			RCL2	3402	
•	83		X	71	
0			0		
0			•	83	
0			2		
5			8		
X	71		6		
R/S	84	Input Barometer, "Hg	X	71	
X	71		R/S	84	Out µg/m^3; In mg/ml
STO1	3301		RCL2	3402	
R/S	84	Input sample Temp °F	X	71	
4			0		
6			•	83	
0			2		
+	61		8		
RCL1	3401		6		
g x⇄y	3507		X	71	
÷	81		R/S	84	Out µg/m^3; In mg/ml
g 1/x	3504		RCL2	3402	
R/S	84	Input Vol. Toluene, ml	X	71	
X	71		0		
STO2	3302		•	83	
R/S	84	In mg/ml	2		
RCL2	3402		8		
X	71		0		
0			X	71	
•	83		R/S	84	Out µg/m^3; In mg/ml
1			RCL2	3402	
4			X	71	
3			0		
X	71		•	83	
R/S	84	Out µg/m^3; In mg/ml	3		
RCL 2	3402		5		
X	71		9		
0			X	71	
•	83		R/S	84	Out µg/m^3; In mg/ml
1			RCL2	3402	
9			X	71	
6			0		
X	71		•	83	
R/S	84	Out µg/m^3; In mg/ml	1		
RCL 2	3402		7		
X	71		1		
0			X	71	
•	83		R/S	84	Out µg/m^3
2			RTN	24	
4					
4					

REGISTERS

R_1 ______
R_2 ______
R_3 ______
R_4 ______
R_5 ______
R_6 ______
R_7 ______
R_8 ______
R_9 ______

LABELS

A ______
B ______
C ______
D ______
E ______
0 ______
1 ______
2 ______
3 ______
4 ______
5 ______
6 ______
7 ______
8 ______
9 ______

FLAGS

1 ______
2 ______

TO RECORD PROGRAM INSERT MAGNETIC CARD WITH SWITCH SET AT W/PRGM

Figure 14. Aldehyde and Ketone concentrations in µg/mℓ.

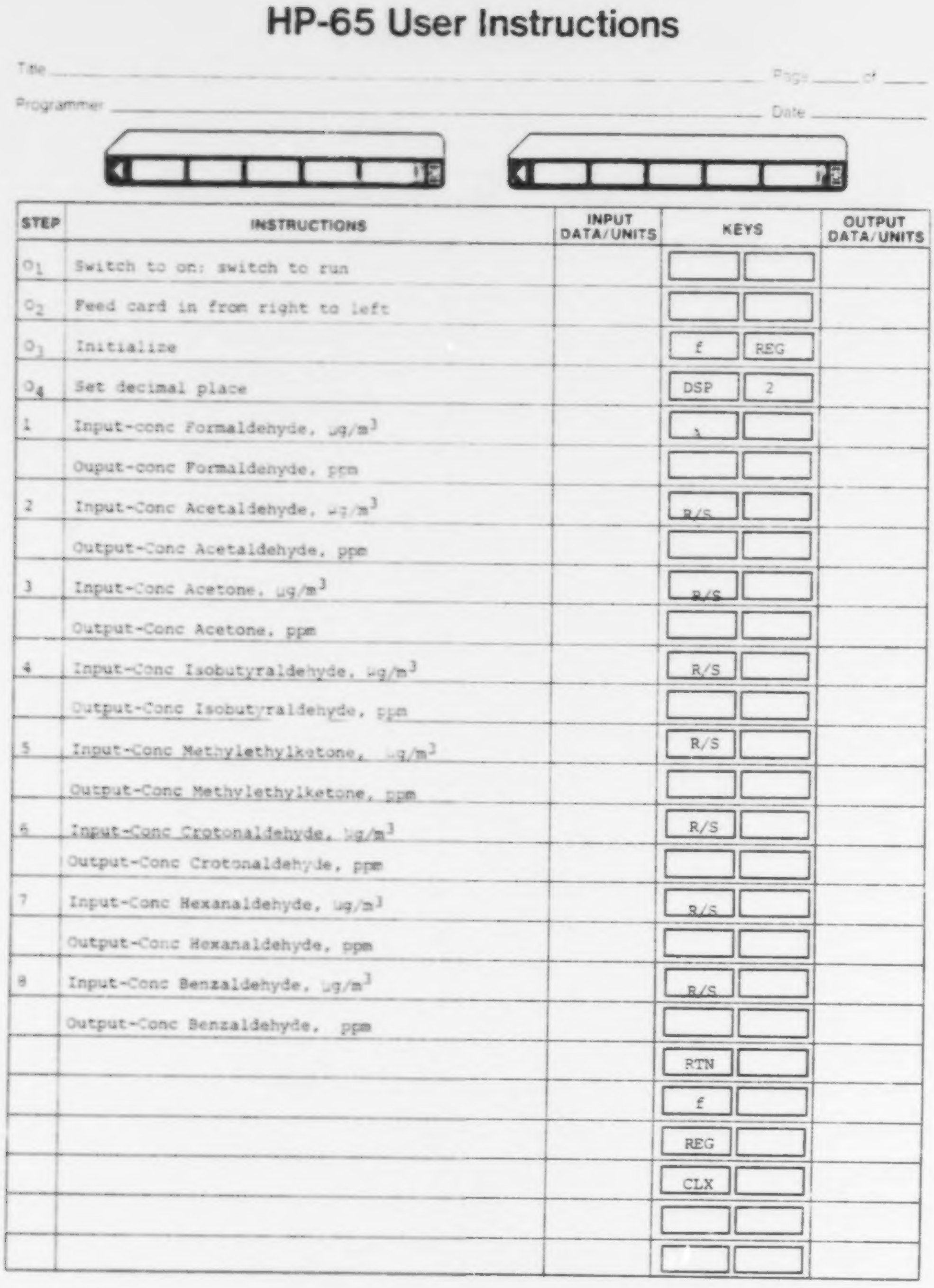
HP-65 User Instructions

Title ________________________________ Page ____ of ____

Programmer ________________________________ Date ________

STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on; switch to run				
0_2	Feed card in from right to left				
0_3	Initialize		f	REG	
0_4	Set decimal place		DSP	2	
1	Input - sample volume, ft^3		A		
2	Input - barometric pressure, "Hg		R/S		
3	Input - Sample Temperature, °F		R/S		
4	Input - Volume Tolune, ml		R/S		
5	Input - Conc. Formaldehyde Der, mg/ml		R/S		
	Output - Conc. Formaldehyde $\mu g/m^3$				
6	Input - Conc. Acetaldehyde Der, mg/ml		R/S		
	Output - Conc. Acetaldehyde $\mu g/m^3$				
7	Input - Conc. Acetone Der, mg/ml		R/S		
	Output - Conc. Acetone, $\mu g/m^3$				
8	Input - Conc. Isobutyraldehyde Der, mg/ml		R/S		
	Output - Conc. Isobutyraldehyde, $\mu g/m^3$				
9	Input - Conc. methylethylketone Der, mg/ml		R/S		
	Output - Conc. methylethylketone, $\mu g/m^3$		.		
10	Input - Conc. Crotonaldehyde Der, mg/ml		R/S		
	Output - Conc. Crotonaldehyde, $\mu g/m^3$				
11	Input - Conc. Hexanaldehyde Der, mg/ml		R/S		
	Output - Conc. Hexanaldehyde, $\mu g/m^3$				
12	Input - Conc. Benzaldehyde Der, mg/ml		R/S		
	Output - Conc. Benzaledhyde $\mu g/m^3$				
			RTN		
			f		(cont'd.)

Figure 14 (Cont'd). Aldehyde and Ketone concentrations in $\mu g/m^3$.



HP-65 User Instructions

Title ______________________________ Page ____ of ____

Programmer ______________________________ Date ________

STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on: switch to run				
0_2	Feed card in from right to left				
0_3	Initialize		f	REG	
0_4	Set decimal place		DSP	2	
1	Input-conc Formaldehyde, μg/m^3		↑		
	Ouput-conc Formaldehyde, ppm				
2	Input-Conc Acetaldehyde, μg/m^3		R/S		
	Output-Conc Acetaldehyde, ppm				
3	Input-Conc Acetone, μg/m^3		R/S		
	Output-Conc Acetone, ppm				
4	Input-Conc Isobutyraldehyde, μg/m^3		R/S		
	Output-Conc Isobutyraldehyde, ppm				
5	Input-Conc Methylethylketone, μg/m^3		R/S		
	Output-Conc Methylethylketone, ppm				
6	Input-Conc Crotonaldehyde, μg/m^3		R/S		
	Output-Conc Crotonaldehyde, ppm				
7	Input-Conc Hexanaldehyde, μg/m^3		R/S		
	Output-Conc Hexanaldehyde, ppm				
8	Input-Conc Benzaldehyde, μg/m^3		R/S		
	Output-Conc Benzaldehyde, ppm				
			RTN		
			f		
			REG		
			CLX		

Figure 15. Aldehyde and Ketone concentrations in ppm.

HP-65 Program Form

Title ______________________________ Page ___ of ___

SWITCH TO W/PRGM PRESS f PRGM TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS	KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23				In conc μg/m³
A	11	In conc μg/m³	2		
1			4		
2			1		
4			5		
9			÷	81	
÷	81		R/S	84	Out conc ppm
R/S	84	Out conc ppm	RTN	24	
		In conc μg/m³			
1					
8					
3					
2					
÷	81				
R/S	84	Out conc ppm			
		In conc μg/m³			
2					
4					
1					
6					
÷	81				
R/S	84	Out conc ppm			
		In conc μg/m³			
3					
0					
0					
0					
÷	81				
R/S	84	Out conc ppm			
		In conc μg/m³			
3					
0					
0					
0					
÷	81				
R/S	84	Out conc ppm			
		In conc μg/m³			
2					
9					
1					
6					
÷	81				
R/S	84	Out conc ppm			
		In conc μg/m³			
4					
1					
6					
6					
÷	81				
R/S	84	Out conc ppm			

REGISTERS

R_1 ______

R_2 ______

R_3 ______

R_4 ______

R_5 ______

R_6 ______

R_7 ______

R_8 ______

R_9 ______

LABELS

A ______
B ______
C ______
D ______
E ______
0 ______
1 ______
2 ______
3 ______
4 ______
5 ______
6 ______
7 ______
8 ______
9 ______

FLAGS

1 ______
2 ______

TO RECORD PROGRAM INSERT MAGNETIC CARD WITH SWITCH SET AT W/PRGM

Figure 15 Cont'd). Aldehyde and Ketone concentrations in ppm.

Sample Calculation

Assume exhaust samples were collected in glass impingers for each portion of a three bag 1975 FTP. Raw data for these tests is presented in Figure 16. Calculations were performed using the HP-65 programs and manual calculations.

Manual calculation for driving cycle FTP-1:

$$\mu g/m^3 \text{ formaldehyde} = \frac{\text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \text{mol. wt. carbonyl}}{P_{\text{exp}}\ (\text{"Hg}) \times V_{\text{exp}}\ (\text{ft}^3)}$$

$$\times \frac{1000\ \mu\text{g/mg} \times T_{\text{exp}}\ ({}^\circ\text{R}) \times 29.92\text{" Hg}}{528^\circ\text{R}}$$

$$\times \frac{35.31\ \text{ft}^3/\text{m}^3}{\text{mol. wt. derivative}}$$

$$= \frac{0.186\ \text{mg/m}\ell \times 2\text{m}\ell \times 30.03\ \text{g/mole} \times 1000\ \mu\text{g/mg}}{29.80\text{" Hg} \times 3.196\ \text{ft}^3 \times 528^\circ\text{R}}$$

$$\times \frac{535^\circ\text{R} \times 29.92\text{" Hg} \times 35.31\ \text{ft}^3/\text{m}^3}{201.15\ \text{g/mole}}$$

$$= 597.5\ \mu\text{g/m}^3$$

$$\text{ppm formaldehyde} = \mu\text{g/m}^3 \div \text{density } \mu\text{g/m}\ell$$

$$\text{density } \mu\text{g/m}\ell = \frac{\text{mol. wt. (formaldehyde)} \times 1000}{24.04\ell}$$

$$\text{mol. wt. formaldehyde} = 30.03\ \text{g/mole}$$

$$\text{density} = \frac{30.03\ \text{g/mole} \times 1000}{24.04\ell} = 1249\ \mu\text{g/m}\ell$$

$$\text{ppm} = 597.5\ \mu\text{g/m}^3 \div 1249\ \mu\text{g/m}\ell = 0.478\ \text{m}\ell/\text{m}^3 = 0.478\ \text{ppm}$$

The calculations for acetaldehyde, acetone, isobutyraldehyde, methylethyketone, crotonaldehyde, hexanaldehyde, and benzaldehyde are carried out in the same manner by substituting the appropriate derivative concentrations and molecular weights into the above formulas. These calculations give the following concentrations:

acetaldehyde, 561 μg/m^3 and 0.306 ppm
acetone, 663 μg/m^3 and 0.274 ppm
isobutyraldehyde, 141 μg/m^3 and 0.047 ppm
methylethylketone, 630 μg/m^3 and 0.210 ppm
crotonaldehyde, 541 μg/m^3 and 0.186 ppm
hexanaldehyde, 250 μg/m^3 and 0.060 ppm

SWRI PROJECT NO.________TEST NO.__________TEST DATE:__________VEHICLE:_________
FUEL:_______CVS NO._______TUNNEL SIZE:________DRIVER:___________MILES:____________
SAMPLE COLLECTION BY:__________CHEMICAL ANALYSIS BY:_______CALCULATIONS BY:_______
GENERAL COMMENTS:____

Test No.	1	2	3	4	5	6
Driving Cycle	FTP-1	FTP-2	FTP-3	SET-7	HFET	NYCC
Volume, Ft^3	3.196	1.625	2.010	3.730	8.241	1.070
B.P., "Hg	29.90	30.02	29.02	29.25	29.95	29.50
Temp. °F	75	80	96	85	83	89
Vol. Toluene ml	2	2	2	2	2	2
Formaldehyde Der Conc mg/ml	0.186	0.105	0.201	0.312	0.732	0.142
Formaldehyde Conc μg/m^3	598	665	1100	891	921	1410
Formaldehyde Conc ppm	0.479	0.532	0.881	0.713	0.737	1.130
Acetaldehyde Der Conc mg/ml	0.127	0.092	0.157	0.282	0.612	0.102
Acetaldehyde Conc μg/m^3	559	798	1170	1100	1060	1390
Acetaldehyde Conc ppm	0.305	0.436	0.639	0.600	0.579	0.759
Acetone Der Conc mg/ml	0.121	0.098	0.161	0.285	0.595	0.105
Acetone Conc μg/m^3	663	1060	1500	1390	1280	1780
Acetone Conc ppm	0.274	0.439	0.621	0.575	0.530	0.737
I-Bu Aldehyde Der Conc mg/ml	0.022	0.011	0.028	0.023	0.051	0.009
I-Bu Aldehyde Conc μg/m^3	141	139	305	131	128	179
I-Bu Aldehyde Conc ppm	0.047	0.046	0.102	0.044	0.043	0.060
MeEt Ketone Der Conc mg/ml	0.098	0.084	0.097	0.198	0.252	0.075
MeEt Ketone Conc μg/m^3	630	1060	1060	1130	634	1490
MeEt Ketone Conc ppm	0.210	0.353	0.353	0.377	0.211	0.497
Cro-Aldehyde Der Conc mg/ml	0.086	0.074	0.076	0.105	0.286	0.072
Cro-Aldehyde Conc μg/m^3	541	917	811	587	705	1400
Cro-Aldehyde Conc ppm	0.186	0.314	0.278	0.201	0.242	0.480
Hex-Aldehyde Der Conc mg/ml	0.031	0.018	0.030	0.027	0.078	0.011
Hex-Aldehyde Conc μg/m^3	250	286	411	194	246	275
Hex-Aldehyde Conc ppm	0.060	0.069	0.099	0.047	0.059	0.066
Benzaldehyde Der Conc mg/ml	0.093	0.081	0.097	0.121	0.232	0.081
Benzaldehyde Conc μg/m^3	775	1330	1370	897	757	2090
Benzaldehyde Conc ppm	0.176	0.301	0.310	0.203	0.171	0.473

Figure 16. Aldehyde Collection Sheet.

Benzaldehyde, 775 g/m^3 and 0.176 ppm.

Note: The values used in these calculations are picked from a range of temperatures, derivative concentrations, etc. to validate the calculations and may not be representative of expected raw data. The calculations are presented to confirm the manual and HP-65 calculations give the same results. This was confirmed for six sets of calculations.

REFERENCES

This procedure is taken from the procedure: "Oxygenated Compounds in Automobile Exhaust-Gas Chromatograph Procedure" by Fred Stump, ESRL, Environmental Protection Agency, Research Triangle Park, North Carolina.

APPENDIX C

ORGANIC AMINE PROCEDURE

THE MEASUREMENT OF ORGANIC AMINES IN EXHAUST

The measurement of organic amines (monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, and triethylamine) in exhaust is accomplished by bubbling the exhaust through glass impingers containing dilute sulfuric acid. The amines are complexed by the acid to form stable sulfate salts which remain in solution. The exhaust sample is collected continuously during the test cycle. A portion of this solution is injected into a gas chromatograph equipped with an ascarite loaded pre-column and a nitrogen phosphorus detector (NPD). External amine standards in dilute sulfuric acid are used to qualify the results. Detection limits for this procedure are on the order of 0.01 ppm-0.05 ppm.

LIST OF EQUIPMENT AND REAGENTS

The equipment and reagents for the analysis of the organic amines are divided into two groups. The first involves the sample acquisition and the second the instrumental analysis of the sample once it has been obtained. Manufacturer, stock number and any pertinent descriptive information are listed.

Sampling

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.
2. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 l/min range.
3. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 l/min.
4. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.
5. Regulating valve, Nupro 4MG, stainless steel.
6. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16: OD x 1/8" ID.
7. Teflon solenoid valve, The Fluorocarbon Company, Model DV2-144NCA1.
8. Drying tube, Analabs Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.

9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.

10. Digital readout for dry gas meter.

11. Miscellaneous electrical switches, lights, wirings, etc.

12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.

13. Iron/Constantan type J single thermocouple qith 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.

14. 30 ml polypropylene sample storage bottles, Nalgene Labware, Catalog #2006-0001.

15. Sulfuric Acid, H_2SO_4, formula weight - 98.08, Certified 1N by Fisher Scientific Company, #SO-A-212.

16. Class A, 10 mℓ volumetric pipet.

17. Class A, 1000 mℓ volumetric flask.

Instrumental Analysis

1. 10 μl syringe, Pressure-Lok, Precision Sampling Corporation.

2. Perkin-Elmer Model 3920 B gas chromatograph equipped with an ascarite loaded pre-column, a teflon interface, and a nitrogen phosphorus detector (NPD).

3. Soltec Model B-281 1 mv recorder.

4. Hewlett-Packard Model 3354 gas chromatograph computer system with remote teletype printout.

5. Glass insert for 1/8" and 1/4" heated injectors (used as pre-column), Perkin-Elmer, #009-1958.

6. Ascarite, 20-30 mesh, Arthur H. Thomas Company, Catalog #C049-U86.

7. Teflon tubing (used for interface in gas chromatograph), Analabs Inc., 1/6" OD x 0.03" ID, #HGC-024.

8. Methylamine Hydrochloride, $CH_3NH_2 \cdot HCl$, formula weight = 67.52, crystals, Eastman #116.

9. Dimethylamine Hydrochloride, $(CH_3)_2NH \cdot HCl$, formula weight = 81.55, crystals, Eastman #94.

10. Trimethylamine Hydrochloride, $(CH_3)_3N \cdot HCl$, formula weight = 95.57, crystals, Eastman #265

11. Ethylamine Hydrochloride, $C_2H_5NH_2 \cdot HCl$, formula weight = 81.55, crystals, Eastman #731

12. Diethylamine Hydrochloride, $(C_2H_5)_2NH \cdot HCl$, formula weight = 109.6, crystals, Eastman #2090

13. Triethylamine Hydrochloride, $(C_2H_5)_3N \cdot HCl$, formula weight = 137.65, crystals, Eastman #8535.

Preparation of Absorbing Solution

The absorbing solution (0.01 N H_2SO_4) is prepared by diluting 10 ml of 1 N sulfuric acid (certified Fishcer Scientific Company) to 1 liter with deionized water.

Preparation of Ascarite Pre-Column

The ascarite pre-column is prepared by packing a Perkin-Elmer glass insert for a heated injector block with 20-30 mesh ascarite and plugging both ends with 1/4" of glass wool. The packed pre-column is shown in Figure 1. This packed pre-column is then inserted into the heated injector and held in place against the column with a spring loaded metal tube and the septum cap.

Preparation of Primary Standards

The primary standards for the organic amines are prepared by dissolving a weighed amount of the amine-hydrochloric acid salt in 0.01 N sulfuric acid and diluting the resulting mixture to the proper volume with 0.01 N sulfuric acid. Standards less that 10 ppm are prepared by diluting higher concentraion standards with 0.01 N sulfuric acid.

SAMPLING SYSTEM

A glass impinger containing 25 ml of 0.01 N sulfuric acid is used to collect exhaust samples for the analysis of the organic amines. A flow schematic of the sample collection system is shown in Figure 2. The single glass impinger is sufficient to collect 99 percent+ of the organic amines. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. The dry gas meter determines the total flow through the impinger during a given driving cycle. The sample pump is capable of pulling a flow rate of 4 liters/minute. A drier is included to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter allows continuous monitoring of the sample flow to insure proper flow rates during the sampling. Several views of the sampling system are shown in Figure 3.

ANALYTICAL PROCEDURE

The analysis of the organic amines (monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, and triethylamine) is accomplished by trapping the amines in sulfuric acid and analyzing the sample

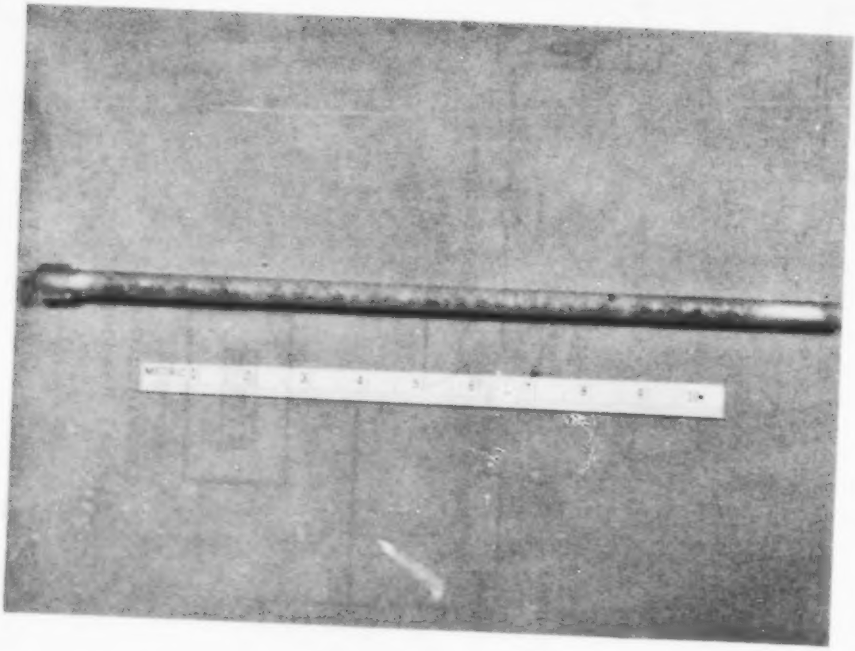


Figure 1. Ascarite pre-column.

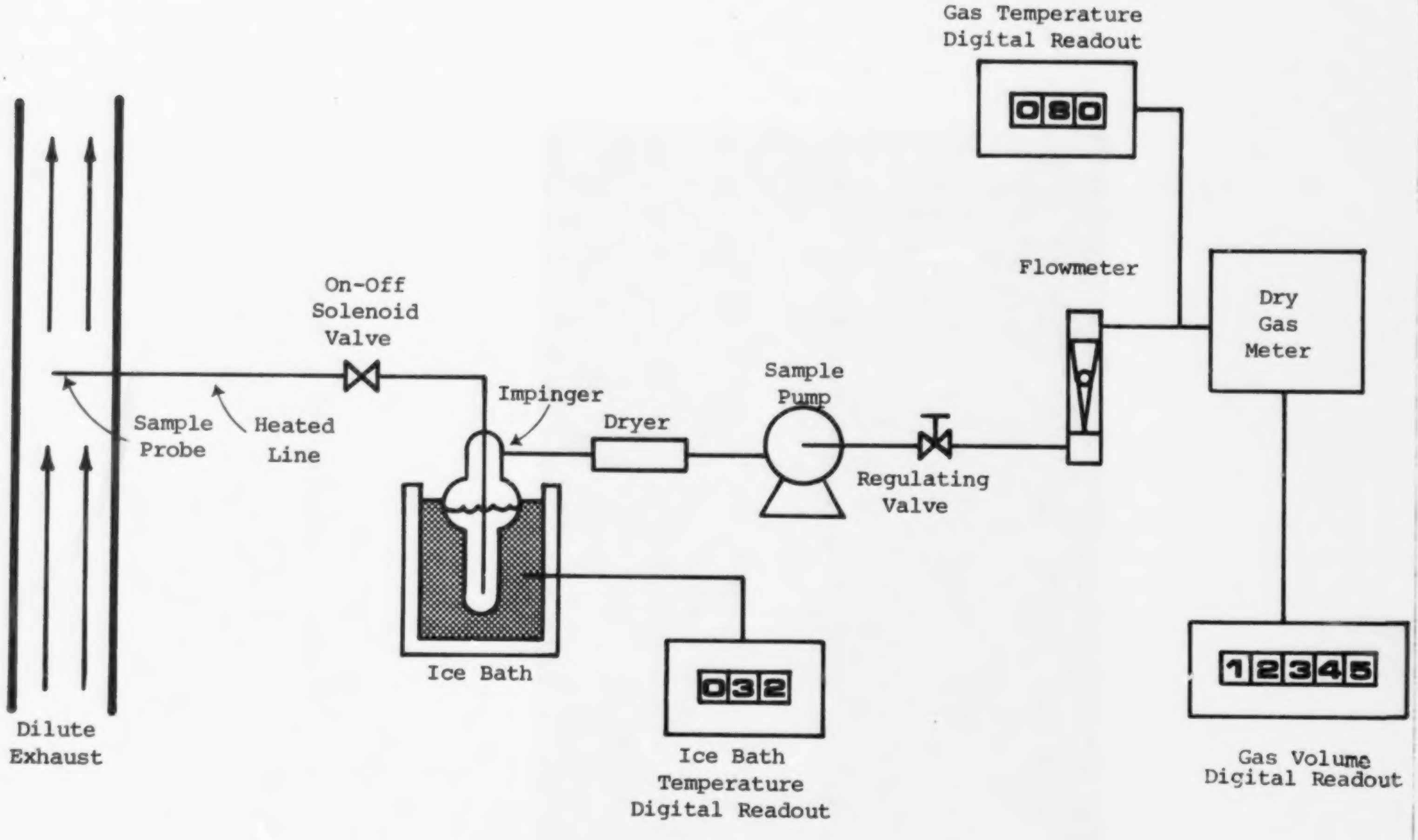
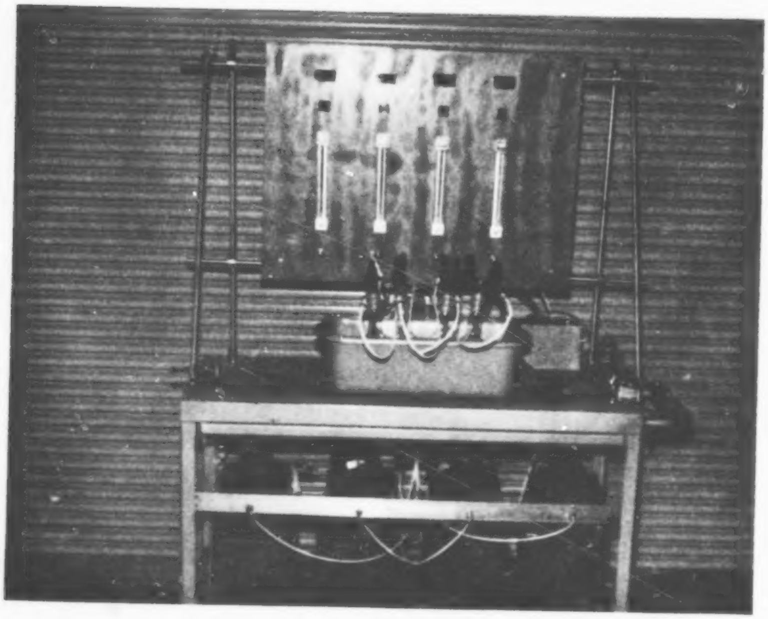
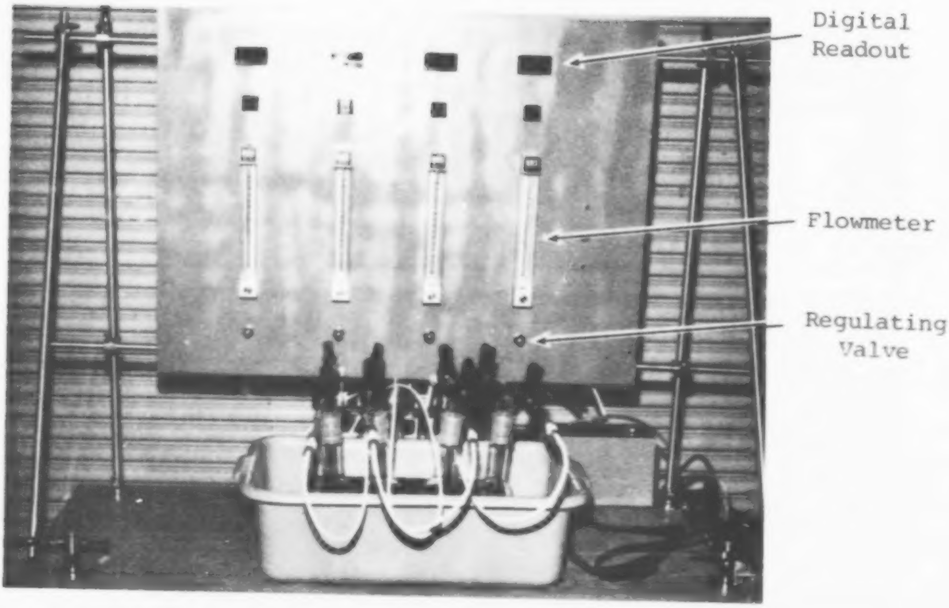

Gas Temperature Digital Readout
080
On-Off Solenoid Valve
Flowmeter
Dry Gas Meter
Sample Pump
Impinger
Dryer
Sample Probe
Heated Line
Regulating Valve
Ice Bath
032
12345
Dilute Exhaust
Ice Bath Temperature Digital Readout
Gas Volume Digital Readout

Figure 2. Organic amines sample collection flow schematic.

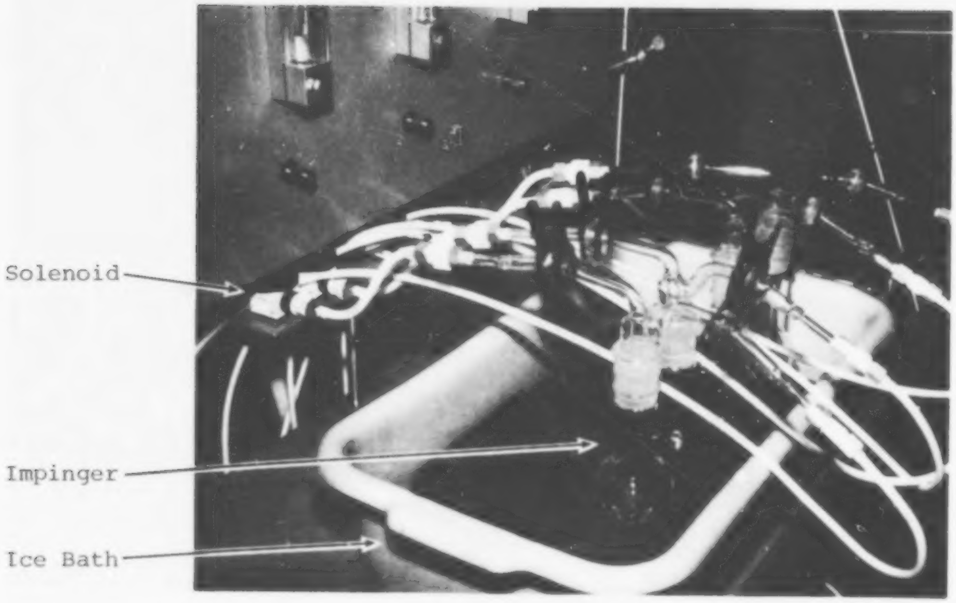


Front View

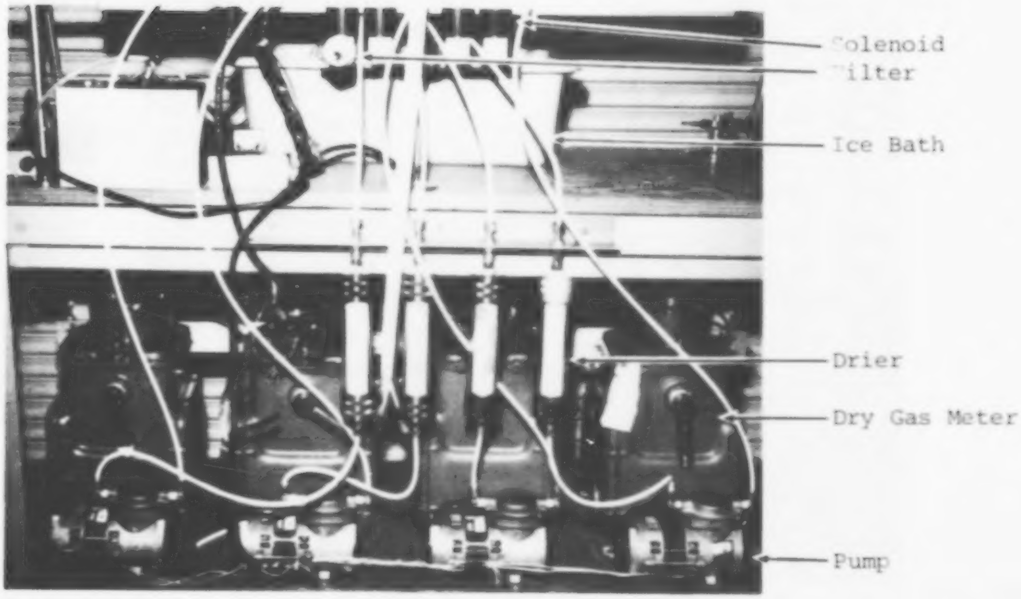

Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 3. Organic Amines sampling system.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 3 (Cont'd). Organic Amines sampling system.

with a gas chromatograph equipped with a NPD. The NPD is highly sensitive to organic nitrogen compounds and relatively insensitive to inorganic nitrogen compounds. The analysis flow schematic for the organic amines is shown in Figure 4. A detailed description of the procedure follows.

For the analysis of the organic amines, dilute exhaust is bubbled through a single glass impinger containing 25 mℓ of 0.01 N sulfuric acid. This sulfuric acid solution traps 99 percent+ of the organic amines as their sulfate salts. The temperature of the impinger is maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4 ℓ/min. Upon completion of each driving cycle, the impinger is removed and the contents are transferred to a 30 mℓ polypropylene bottle and capped. The amines, as their sulfate salts, can be stored in solution for long periods of time without decomposition.

A Perkin-Elmer 3920B gas chromatograph equipped with an ascarite loaded pre-column, a teflon interface, and a nitrogen phosphorus detector (NPD) is used to analyze the sample. A 10 μℓ portion of the sample is injected into the gas chromatograph (GC). In the ascarite pre-column the amines are released from their sulfate salts into the GC column. The column is a 6" X 4 mm glass column containing Carbopack B coated with 4 percent Carbowax 20 M and 0.8 percent KOH. The column effectively separates the amines, with the exception of ethylamine and dimethylamine which are reported together as total C_2H_7N. The carrier gas is helium which flows through the column at a rate of 30 mℓ/min. The column temperature is 130°C for 4 minutes and then programed to 170°C at a rate of 32° a minute. In a chromatogram of a standard sample containing all six of the amines, Figure 5, the first peak is momomethylamine, followed by the combined peak of dimethylamine and monoethylamine, C_2H_7N, and then by trimethylamine, diethylamine, and triethylamine. The peak areas are compared to standard solutions. Figure 6 shows the analytical system with gas chromatograph, detector, integrator, and recorder.

CALCULATIONS

This procedure has been developed to provide the user with the concentration of the organic amines (monomethylamine, total dimethylamine and monoethylamine as C_2H_7N, trimethylamine, diethylamine and triethylamine) in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm for each of the amines. The equations for determining the concentrations in $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F, and pressure, 29.92"Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

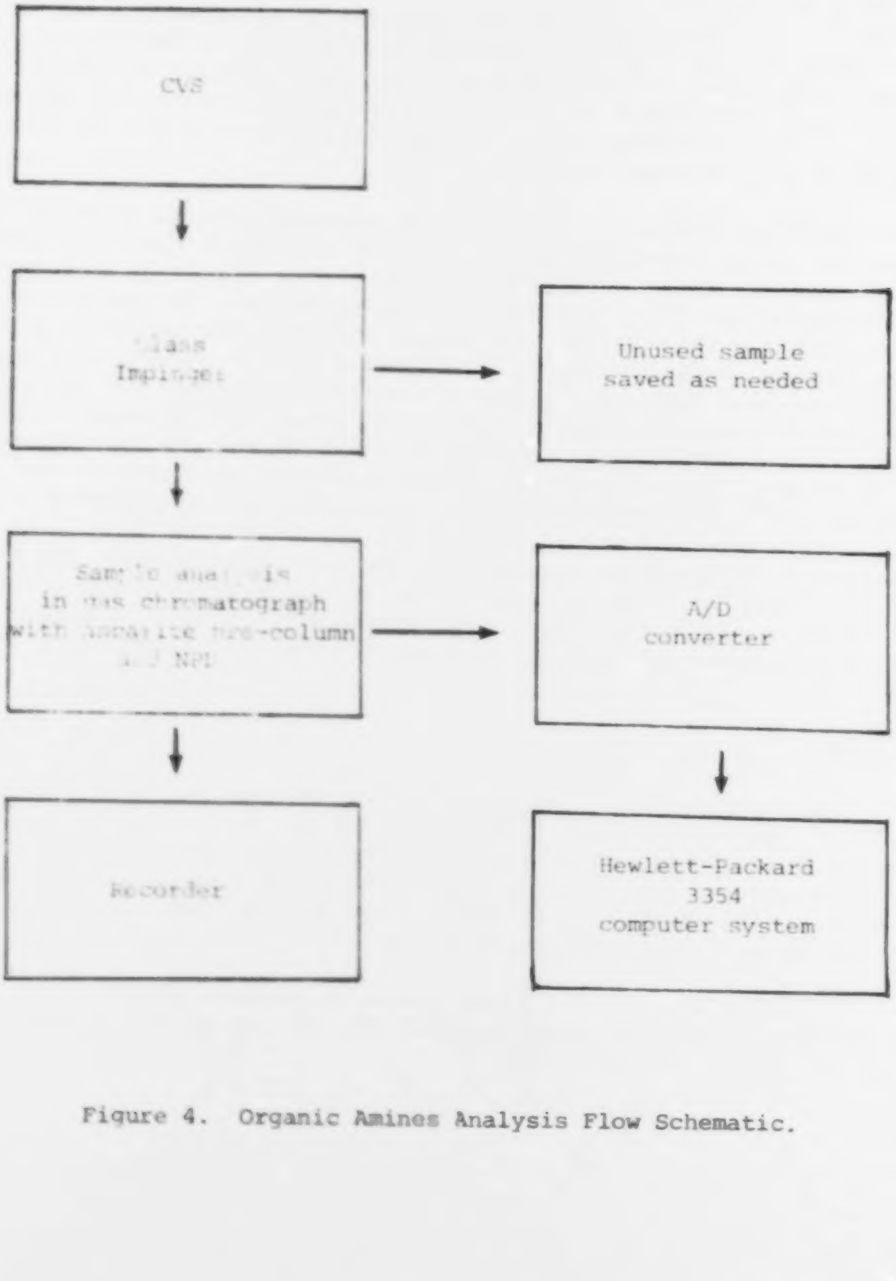

CVS
Glass Impinger
Unused sample saved as needed
Sample analysis in gas chromatograph with Ascarite pre-column and NPD
A/D converter
Recorder
Hewlett-Packard 3354 computer system

Figure 4. Organic Amines Analysis Flow Schematic.

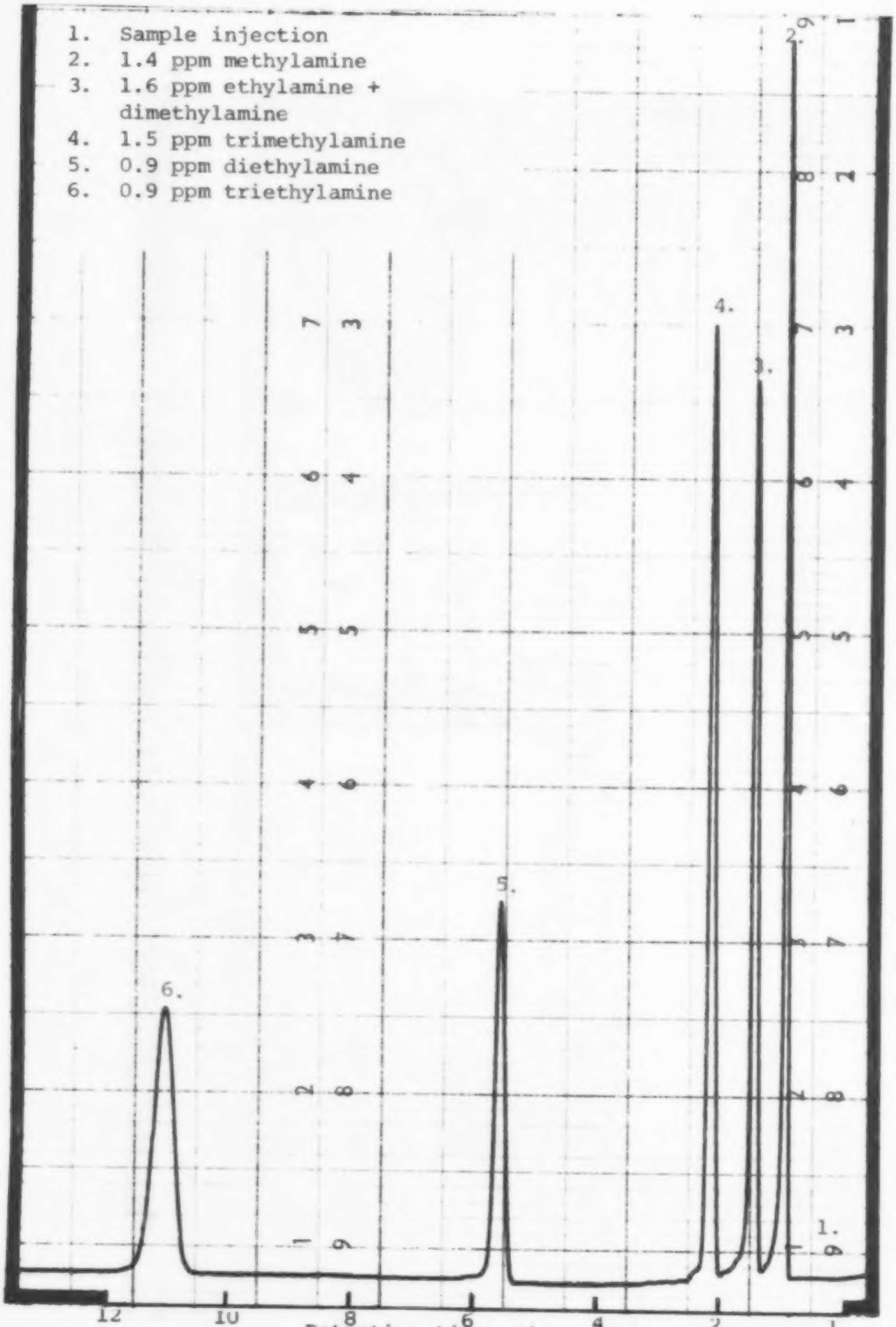


Figure 5. Chromatogram of amine standard.

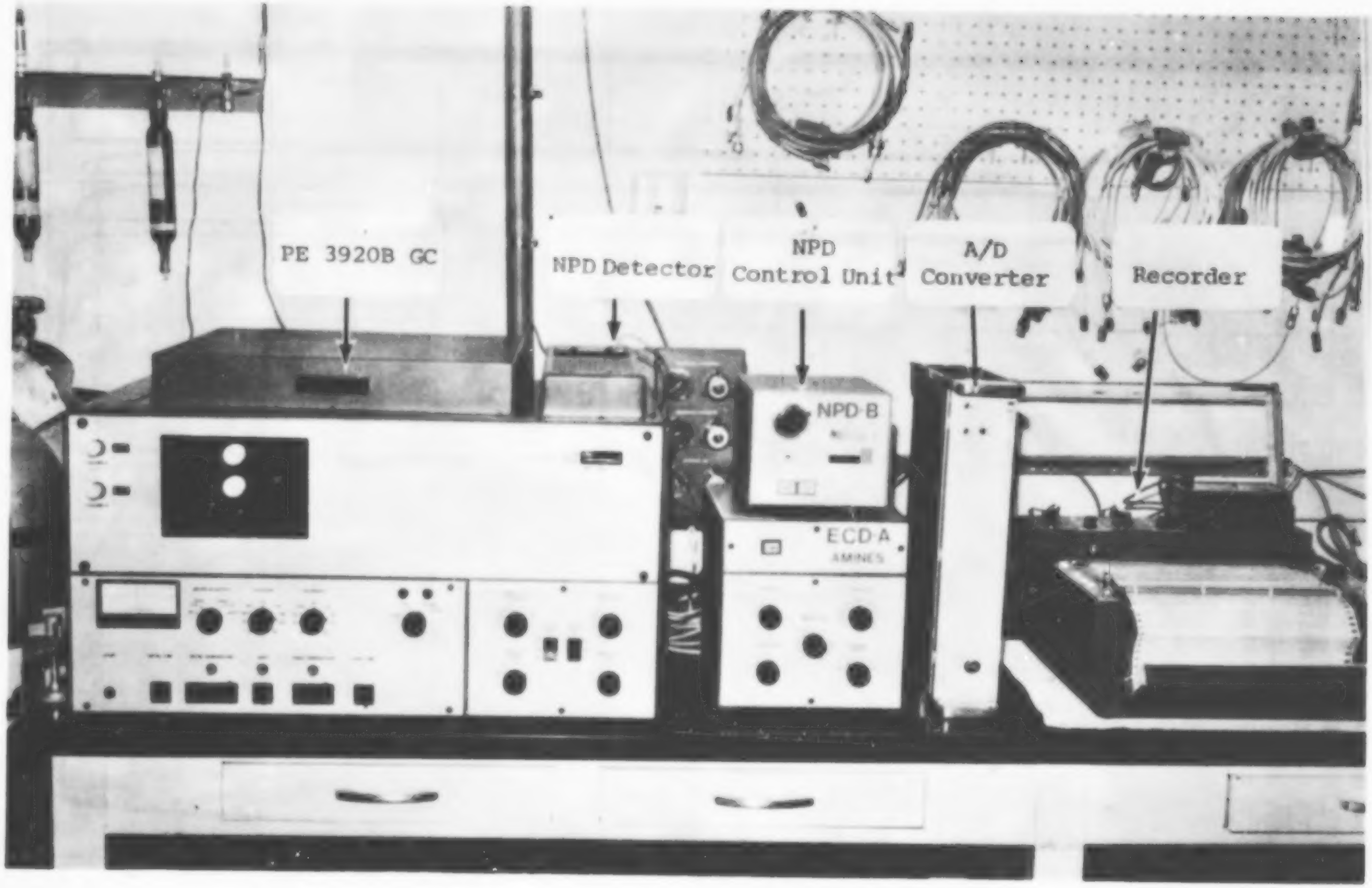

PE 3920B GC
NPD Detector
NPD
Control Unit
A/D
Converter
Recorder
NPD-B
ECD-A
AMINES

Figure 6. Total amine analytical system.

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92"Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92"Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{"Hg}}$$

The next step converts the volume from cubic feet to cubic meters by use of the converstion factor 1 cubic meter is equal to 35.31 cubic feet.

$$V_{corr}(m^3) = \frac{P_{exp}(\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°}{T_{exp} \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}$$

(Equation 1)

The next step is to find the concentration of each of the amines in μg/mℓ. Since the gas chromatograph NPD has a linear response in the concentration of concern, then the following equation holds.

$$\frac{C_{sam}\ (\mu g/m\ell)}{A_{sam}} = \frac{C_{std}\ (\mu g/m\ell)}{A_{std}}$$

C_{sam} = concentration of the sample in μg/mℓ
A_{sam} = GC peak area of sample in relative units
C_{std} = concentration of the standard in μg/mℓ
A_{std} = GC peak area of standard in relative units

Solving for C_{sam} gives:

$$C_{sam}(\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam}}{A_{std}}$$

The $C_{sam}(\mu g/m\ell)$ in solution is corrected for any necessary dilution by multiplying by the dilution factor, D.F.

$$C_{sam}(\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F.}{A_{std}}$$

To obtain the total amount in µg of each amine in the absorbing solution, the absorbing reagent volume is multiplied by the concentration to give:

$$\mu g \text{ sample} = C_{sam}\ (\mu g/m\ell) \times \text{Abs. Vol. } (m\ell)$$

$$= \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{A_{std}}$$

(Equation 2)

To obtain µg sample/m^3, Equation 2 is divided by Equation 1 to give:

$$\mu g \text{ samp}/m^3 = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{A_{std} \times P_{exp}\ (\text{"Hg}) \times 528^\circ}$$

$$\times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ (ft^3/m^3)}{V_{exp}\ (ft^3)}$$

(Equation 3)

To find the concentration of each amine in ppm, the densities of the amines are needed. At 29.92"Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation

$$\frac{V}{T} = \frac{V_1}{T_1}$$

V_1 = 22.4ℓ
T_1 = 32°F + 460 = 492°R
V = volume at 68°F
T = 68°F + 460 = 528°R

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04 at 68°F, the density can be found in g/ℓ by dividing the molecular weight in g/mole by 22.04 ℓ/mole

$$\text{den } (g/\ell) = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}}$$

The density in μg/mℓ can be found by converting g to μg and ℓ to mℓ as follows:

$$\text{den } \mu g/m\ell = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}} \times \frac{1 \times 10^6 \mu g/g}{1 \times 10^3 m\ell/\ell} = \frac{\text{mol. wt.} \times 1000}{24.04}$$

(Equation 4)

To obtain the concentration of each amine in ppm, the concentration in $\mu g/m^3$ is divided by the density in μg/mℓ

$$\text{ppm} = \mu g/m^3 \div \mu g/m\ell = \frac{m\ell}{m^3}$$

Using Equations 3 and 4 gives the ppm concentration in the form of the raw data.

$$\text{ppm} = \frac{24.04(\ell) \times C_{std}\ (\mu g/m\ell) \times A_{sam} \times \text{D.F.} \times \text{Abs. Vol. } (m\ell)}{\text{Mol. Wt. (g/mole)} \times 1000 \times A_{std} \times P_{exp}\ (\text{"Hg})}$$

$$\times \frac{T_{exp}(°R) \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528°R \times V_{exp}\ (ft^3)}$$

(Equation 5)

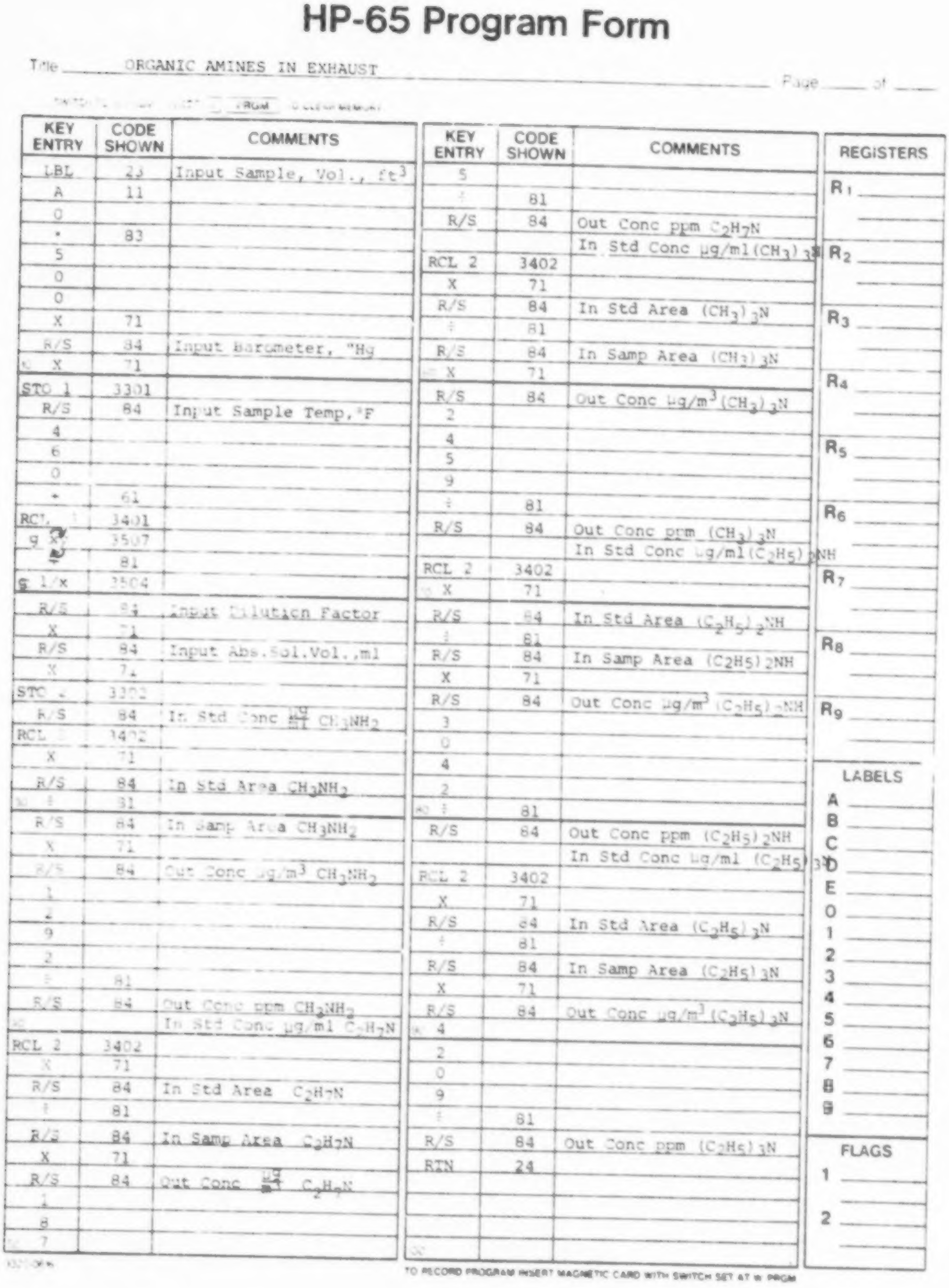
At this point, the concentration can be expressed in $\mu g/m^3$ (Equation 3) and ppm (Equation 5) at 68°F and 29.92"Hg from the raw data.

Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period a Hewlett-Packard 65 program was developed to calculate the organic amine concentrations in $\mu g/m^3$ and ppm from the raw data. This program is presented in Figure 7.

Sample Calculation

Assume exhaust samples were collected in glass impingers for each portion of a three-bag 1975 FTP. Raw data for these tests are presented in Figure 8. Calculations were performed using the HP-65 program and manual calculations.



HP-65 Program Form

Title ORGANIC AMINES IN EXHAUST Page ____ of ____

KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23	Input Sample, Vol., ft^3
A	11	
0		
•	83	
5		
0		
0		
X	71	
R/S	84	Input Barometer, "Hg
X	71	
STO 1	3301	
R/S	84	Input Sample Temp, °F
4		
6		
0		
+	61	
RCL 1	3401	
g x⇄y	3507	
÷	81	
g 1/x	3504	
R/S	84	Input Dilution Factor
X	71	
R/S	84	Input Abs.Sol.Vol.,ml
X	71	
STO 2	3302	
R/S	84	In Std Conc $\frac{\mu g}{ml}$ CH_3NH_2
RCL 2	3402	
X	71	
R/S	84	In Std Area CH_3NH_2
÷	81	
R/S	84	In Samp Area CH_3NH_2
X	71	
R/S	84	Out Conc µg/m^3 CH_3NH_2
1		
2		
9		
2		
÷	81	
R/S	84	Out Conc ppm CH_3NH_2
		In Std Conc µg/ml C_2H_7N
RCL 2	3402	
X	71	
R/S	84	In Std Area C_2H_7N
÷	81	
R/S	84	In Samp Area C_2H_7N
X	71	
R/S	84	Out Conc $\frac{\mu g}{m^3}$ C_2H_7N
1		
8		
7		

KEY ENTRY	CODE SHOWN	COMMENTS
5		
÷	81	
R/S	84	Out Conc ppm C_2H_7N
		In Std Conc µg/ml$(CH_3)_3N$
RCL 2	3402	
X	71	
R/S	84	In Std Area $(CH_3)_3N$
÷	81	
R/S	84	In Samp Area $(CH_3)_3N$
X	71	
R/S	84	Out Conc µg/m^3$(CH_3)_3N$
2		
4		
5		
9		
÷	81	
R/S	84	Out Conc ppm $(CH_3)_3N$
		In Std Conc µg/ml$(C_2H_5)_2NH$
RCL 2	3402	
X	71	
R/S	84	In Std Area $(C_2H_5)_2NH$
÷	81	
R/S	84	In Samp Area $(C_2H_5)_2NH$
X	71	
R/S	84	Out Conc µg/m^3 $(C_2H_5)_2NH$
3		
0		
4		
2		
÷	81	
R/S	84	Out Conc ppm $(C_2H_5)_2NH$
		In Std Conc µg/ml $(C_2H_5)_3N$
RCL 2	3402	
X	71	
R/S	84	In Std Area $(C_2H_5)_3N$
÷	81	
R/S	84	In Samp Area $(C_2H_5)_3N$
X	71	
R/S	84	Out Conc µg/m^3 $(C_2H_5)_3N$
4		
2		
0		
9		
÷	81	
R/S	84	Out Conc ppm $(C_2H_5)_3N$
RTN	24	

REGISTERS

R_1 ____
R_2 ____
R_3 ____
R_4 ____
R_5 ____
R_6 ____
R_7 ____
R_8 ____
R_9 ____

LABELS

A ____
B ____
C ____
D ____
E ____
0 ____
1 ____
2 ____
3 ____
4 ____
5 ____
6 ____
7 ____
8 ____
9 ____

FLAGS

1 ____
2 ____

TO RECORD PROGRAM INSERT MAGNETIC CARD WITH SWITCH SET AT W/PRGM

Figure 7. HP-65 program form.

HP-65 User Instructions

Title ______________________ Page ____ of ____

Programmer ______________________ Date ________

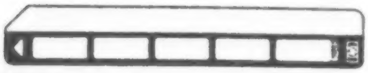
STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on; Switch to run				
0_2	Feed card in from right to left				
0_3	Initialize		f	REG	
0_4	Set decimal place		DSP	2	
1	Input Sample Volume, ft^3		A		
2	Input - Barometric Pressure, "Hg		R/S		
3	Input - Sample Temperature, °F		R/S		
4	Input - Dilution Factor		R/S		
5	Input - Absorbing Reagent Vol., ml		R/S		
6	Input - Standard Conc. μg/ml CH_3NH_2		R/S		
7	Input - Standard area CH_3NH_2		R/S		
8	Input - Sample Area CH_3NH_2		R/S		
	Output - Sample Conc. $\mu g/m^3$ CH_3NH_2		R/S		
	Output - Sample Conc. ppm CH_3NH_2				
9	Input - Standard Conc. μg/ml C_2H_7N		R/S		
10	Input - Standard Area C_2H_7N		R/S		
11	Input - Sample Area C_2H_7N		R/S		
	Output - Sample Conc. $\mu g/m^3$ C_2H_7N		R/S		
	Output - Sample Conc. ppm C_2H_7N				
12	Input - Standard Conc. μg/ml $(CH_3)_3N$		R/S		
13	Input - Standard Area $(CH_3)_3N$		R/S		
14	Input - Sample Area $(CH_3)_3N$		R/S		
	Output - Sample Conc. $\mu g/m^3$ $(CH_3)_3N$		R/S		
	Output - Sample Conc. ppm $(CH_3)_3N$				
15	Input - Standard Conc. μg/ml $(C_2H_5)_2NH$		R/S		
16	Input - Standard Area $(C_2H_5)_2NH$		R/S		

Figure 7 (Cont'd). HP-65 user instructions.

HP-65 User Instructions

Title ______________________________ Page _____ of _____

Programmer ______________________________ Date __________



STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
17	Input - Sample Area $(C_2H_5)_2NH$		R/S		
	Output - Sample Conc. $\mu g/m^3$ $(C_2H_5)_2NH$		R/S		
	Output - Sample Conc. ppm $(C_2H_5)_2NH$				
18	Input - Standard Conc. $\mu g/ml$ $(C_2H_5)_3N$		R/S		
19	Input - Standard Area $(C_2H_5)_3N$		R/S		
20	Input - Sample Area $(C_2H_5)_3N$		R/S		
	Output - Sample Conc. $\mu g/m^3$ $(C_2H_5)_3N$		R/S		
	Output - Sample Conc. ppm $(C_2H_5)_3N$				
			RTN		
			f		
			REG		
			CLX		

Figure 7 (Cont'd). HP-65 User instructions continued.

SWRI PROJECT NO.__________TEST NO.__________TEST DATE:__________VEHICLE:__________
FUEL:_______CVS NO._______TUNNEL SIZE:________DRIVER:___________MILES:___________
SAMPLE COLLECTION BY:__________CHEMICAL ANALYSIS BY:_______CALCULATIONS BY:_______
GENERAL COMMENTS:____

Test No.	1	2	3	4	5	6
Driving Cycle	FTP-1	FTP-2	FTP-3	SET-7	HFET	NYCC
Volume Ft^3	3.196	1.625	2.010	3.730	8.241	1.070
B.P." Hg	29.80	30.02	29.02	29.25	29.95	29.50
Temp°F	75	80	96	85	83	89
Dilution Factor	1	5	10	2	1	1
Absorb. Rea. Vol. Ml	25	25	50	50	75	75
Stan. Conc. CH_3NH_2 µg/ml	0.05	0.10	0.02	1.00	0.10	0.10
Stan. Area CH_3NH_2	1000	2000	3000	10000	4000	5000
Sample Area CH_3NH_2	640	1000	1880	800	2000	2700
Sample Conc. CH_3NH_2 µg/m^3	8.99	138	119	79.9	16.5	141
Sample Conc. CH_3NH_2 ppm	0.007	0.107	0.092	0.062	0.013	0.109
Stan. Conc. C_2H_7N µg/ml	0.10	0.20	0.30	2.00	0.20	0.20
Stan. Area C_2H_7N	1500	3000	6000	15000	2000	3000
Sample Area C_2H_7N	1000	1800	5000	8500	1500	2000
Sample Conc. C_2H_7N µg/m^3	18.7	332	2380	1130	49.5	348
Sample Conc. C_2H_7N ppm	0.010	0.177	1.270	0.603	0.026	0.186
Stan. Conc. $(CH_3)_3N$ µg/ml	0.50	1.00	0.20	2.00	1.50	1.00
Stan. Area $(CH_3)_3N$	1500	3000	4000	2000	1000	2000
Sample Area $(CH_3)_3N$	1020	2800	2100	1600	875	1630
Sample Conc. $(CH_3)_3N$ µg/m^3	95.5	2580	1000	1600	431	2110
Sample Conc. $(CH_3)_3N$ ppm	0.039	1.050	0.407	0.650	0.176	0.865
Stan. Conc. $(C_2H_5)_2NH$ µg/ml	0.90	1.50	0.10	1.00	0.50	0.40
Stan. Area $(C_2H_5)_2NH$	1560	3000	1870	1420	1900	3100
Sample Area $(C_2H_5)_2NH$	1760	4321	2000	1070	1970	2810
Sample Conc. $(C_2H_5)_2NH$ µg/m^3	285	5980	1020	753	162	946
Sample Conc. $(C_2H_5)_2NH$ ppm	0.094	1.970	0.335	0.247	0.253	0.311
Stan. Conc. $(C_2H_5)_3N$ µg/ml	1.60	2.00	0.10	0.50	0.60	0.20
Stan. Area $(C_2H_5)_3N$	3120	1260	4000	6210	3110	5620
Sample Area $(C_2H_5)_3N$	2850	780	3160	3100	2000	4020
Sample Conc. $(C_2H_5)_3N$ µg/m^3	410	3430	753	249	127	373
Sample Conc. $(C_2H_5)_3N$ ppm	0.098	0.814	0.179	0.059	0.030	0.089

Figure 8. Organic Amine sample collection sheet.

Manual calculations for driving cycle FTP-1

$$\mu g/m^3\ CH_3NH_2 = \frac{C_{std}(\mu g/m\ell) \times A_{sam} \times D.F. \times Abs.\ Vol.\ (m\ell)}{A_{std} \times P_{exp}\ (\text{"Hg})} \times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528°R \times V_{exp}\ (ft^3)}$$

$$= \frac{(0.05\ \mu g/m\ell) \times 640 \times 1 \times 25}{1000 \times 29.80\text{"Hg}} \times \frac{(460 + 75) \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528°R \times 3.196\ ft^3}$$

$$= 8.99\ \mu g/m^3$$

$$PPM\ CH_3NH_2 = \mu g/m^3 \div \text{density}\ \mu g/m\ell$$

$$\text{density}\ \mu g/m\ell = \frac{\text{Mol. Wt. } (CH_3NH_2) \times 1000}{24.04\ell}$$

$$\text{Mol. Wt. } CH_3NH_2 = 31.058\ g/mole$$

$$\text{density} = \frac{31.058 \times 1000}{24.04} = 1292\ \mu g/m\ell$$

$$PPM = 8.99\ \mu g/m^3 \div 1292\ \mu g/m\ell = 0.007\ m\ell/m^3 = 0.007\ ppm$$

The calculations for C_2H_7N, $(CH_3)_3N$, and $(C_2H_5)_3N$ are carried out in the same manner by substituting the appropriate standard concentrations, areas and molecular weights into the above formulas. These calculations give the following concentrations: C_2H_7N, 18.7 $\mu g/m^3$ and 0.01 ppm; $(CH_3)_3N$, 0.05 $\mu g/m^3$ and 0.039 ppm; (C_2H_5) NH, 285 $\mu g/m$ and 0.094 ppm; and $(C_2H_5)_3N$, 410 $\mu g/m^3$ and 0.098 ppm.

Note: the values used in these calculations are picked from a range of temperatures, standards, dilution factors, etc. to validate the calculations and may not be representative of expected raw data. These calculations are presented to confirm that manual and HP-65 calculations give the same results. This was confirmed on six sets of calculations.

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APPENDIX D

SULFUR DIOXIDE PROCEDURE

THE MEASUREMENT OF SULFUR DIOXIDE IN EXHAUST

The concentration of SO_2 in automotive exhaust can be determined as sulfate using the ion chromatograph. SO_2 exhaust samples are collected in two glass bubblers, each containing 3 percent hydrogen peroxide. The temperature of the absorbing solution is kept at 0°C by means of an ice water bath. The bubbled samples are then directly analyzed on the ion chromatograph and compared to standards of known sulfate concentrations.

LIST OF EQUIPMENT

The equipment required for the SO_2 determination is divided into four categories: Sampling, Analysis, Water Filteration and Sample preparation. Manufacturer, stock number and any pertinent descriptive information are listed.

Sampling

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.
2. Flowmeters, Brooks Instrument Division, Model 1555, R-2-15-C, sapphire ball, 0-5 lit/min range, graduated 0-15.
3. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.
4. Digital readout for dry gas meter.
5. Sample pump, Thomas, Model #106 CA18 3, 4 lit/min.
6. Drying tube, Analabs Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.
7. Teflon tubing, United States Plastic Corporation, 1/4" OD × 1/8" ID and 5/16" × 3/16" ID.
8. Teflon solenoid valve, The Fluorocarbon Company, Model #DV2-144N Cal.
9. Miscellaneous Teflon nuts, ferrules, unions, tees, connectors and clamps.
10. Miscellaneous electrical switches, lights, wiring, etc.
11. Regulating valve, Nupro 4M6, stainless steel.

12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.

13. 30 mℓ polypropylene sample storage bottles, Nalgene Labware, Catalog #2006-0001.

14. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.

15. Modified 25 mm A-H Microanalysis filter holder, Millipore, Catalog #XX50 025 00.

16. Fluoropore 25 mm filters, Millipore, Catalog #FHLP 025 00, 0.5 micron pore size.

Analysis

1. Conductivity cell, modified Swagelok reducing union, Catalog #SS-200-6-1, approximate volume, 4.5 µl.
2. Conductivity detector, Hall, Tracor 700.
3. Multivoltage recorder, Soltec, Model #B-281 H.
4. Mini-pump, Milton Roy, series 196-0066-033, 46/460 mℓ/hr capacity.
5. Pulse dampener, Glenco Scientific, Catalog #PD 1000.
6. Polyethylene cubitainers, Cole Parmer Instrument Company, Catalog #6100-20, 1 gallon.

Water Filtration

1. Filtration apparatus, Millipore, Catalog #XX 15 047 00.
2. Filters, Millipore, Catalog #GSWP 047 00, 0.22 micron pore size.

Sample preparation

1. 3 cc disposable syringes, Becton-Dickson, Catalog #5585.
2. Class A, 1 mℓ volumetric pipets.
3. Class A, 2 mℓ volumetric pipets.
4. Class A, 3 mℓ volumetric pipets.
5. Class A, 4 mℓ volumetric pipets.
6. Class A, 5 mℓ volumetric pipets.
7. Class A, 10 mℓ volumetric pipets.

8. Class A, 20 mℓ volumetric pipets.

9. Class A, 25 mℓ volumetric pipets.

10. Class A, 50 mℓ volumetric pipets.

11. Class A, 100 mℓ volumetric pipets.

12. Class A, 100 mℓ volumetric flasks.

13. Class A, 1000 mℓ volumetric flasks.

14. Class A, 2000 mℓ volumetric flasks.

15. Mohr pipet, 1 mℓ graduated 1/10.

LIST OF REAGENTS

A list of reagents used in determination of SO_2 is provided indicating purity, manufacturer and catalog number. The function of each reagent in the procedure is also given.

1. Water - deionized and filtered through 0.22 micron filter.

2. Primary standard - Sulfuric acid, H_2SO_4, certified 0.1N, formula weight = 98.08, ACS reagent grade, Fisher Scientific Company #SO-A-212.

3. Absorbant - Stabilized 30 percent hydrogen peroxide, H_2O_2, formula weight = 34.01, analytical reagent grade, Mallinckrodt #5239.

4. Eluent - Sodium bicarbonate, $NaHCO_3$, formula weight = 84.01, ACS analytical reagent grade powder, Mallinckrodt #7412.

5. Eluent - Sodium carbonate, Na_2CO_3, formula weight = 105.99, ACS analytical reagent grade anhydrous power, Mallinckrodt #7521.

6. Regenerant - Sulfuric acid, H_2SO_4, formula weight = 98.08, ACS analytical reagent grade, Mallinckrodt #2876.

PREPARATION OF REAGENTS

Water is prepared by filtering deionized water through a 0.22 micron Millipore filter and storing in polyethylene bottles. All solutions and dilutions are made up to volume with water prepared in the above manner.

Primary Standard

The stock solution is prepard by diluting 20 mℓ of certified 0.1N H_2SO_4(4800 $\frac{\mu g\ SO_4^{-2}}{m\ell}$) to 1000 mℓ with water. The resulting solution contains

$96.0 \frac{\mu g\ SO_4^{-2}}{m\ell}$. More dilute standards are prepared by pipetting 0.5, 1, 1.5, 2, 3, 4, 8, 10, 20, 30, 40, 50, 60, 70, 80, and 90 mℓ of the stock solution into 100 mℓ volumetric flasks and making up to volume. These standards remain stable for at least fourteen weeks. All glassware used in the preparation of standards should be washed with 1:1 (v:v) nitric acid and then rinsed copiously with tap water with a final rinse of filtered deionized water.

Absorbing Solution (3 percent H_2O_2)

100 mℓ of 30 percent H_2O_2 is diulted to 1 liter with water.

Eluent (0.003 M $NaHCO_3$ + 0.0024 M Na_2CO_3)

Concentrated stock solutions of sodium bicarbonate and sodium carbonate are made up. For 0.6 M $NaHCO_3$, 50.41g is diluted to 1000 mℓ with water. 0.48 M $NaHCO_3$, is prepared by diluting 50.88g of the solid to 1 liter with water. The carbonate solution used as the eluent is made up by pipetting 10 mℓ of each stock solution into a 2 lit volumetric flask and diluting to the mark with water.

Regenerant (1 N H_2SO_4)*

56 mℓ of 95 percent H_2SO_4 is diluted to 2 liters with water.

*A total of 4 liters of each of these solutions are prepared to fill the 4 liter reservoirs in the chromatograph.

SAMPLING SYSTEM

The dilute automotive exhaust sample first passes through a fluoropore filter after which its flow is controlled by an on/off Teflon solenoid valve. See Figure 1. When in the "on" position the gas continues on through the impingers where SO_2 is oxidized to SO_4^{-2} in a 3 percent hydrogen peroxide solution maintained at 0°C by an ice water bath. Two sets of bubblers are required to retain 99 percent of total SO_4^{-2} collected. After reaction the gas enters a molecular sieve-silica gel dryer where moisture is removed. The gas is then drawn by a Thomas sample pump through a Singer dry gas meter. The gas flow through the meter is controlled by a Nupro regulating valve and the flowrate is measured by a Brooks flowmeter. The dry gas meter is equipped with a thermocouple and two digital readouts for temperature (°F) and volume (ft^3) measurement. Several views of the sampling system are illustrated in Figure 2.

PROCEDURE

Dilute exhaust is collected in two bubblers, each containing 25 mℓ of 3 percent H_2O_2. The temperature is maintained at 0-5°C by an ice water bath and the flowrate is adjusted to 4 lit/min. After sampling is completed, the absorbing solution in each bubbler is transferred to a 30 mℓ polypropylene

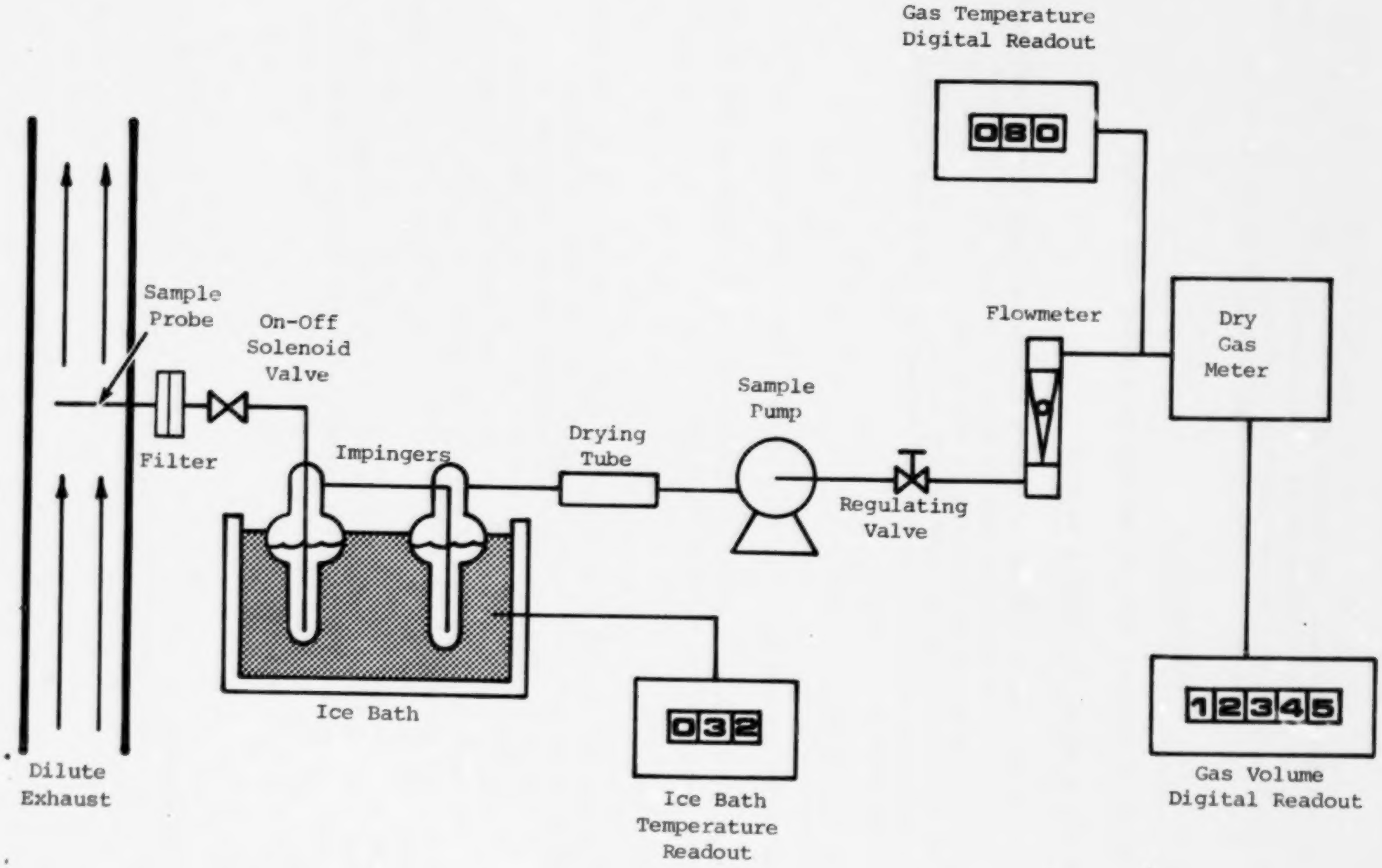
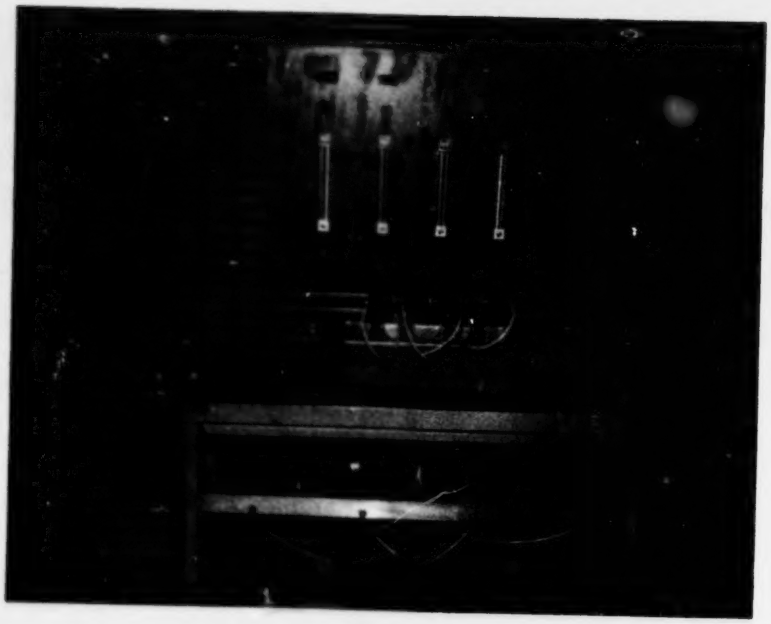
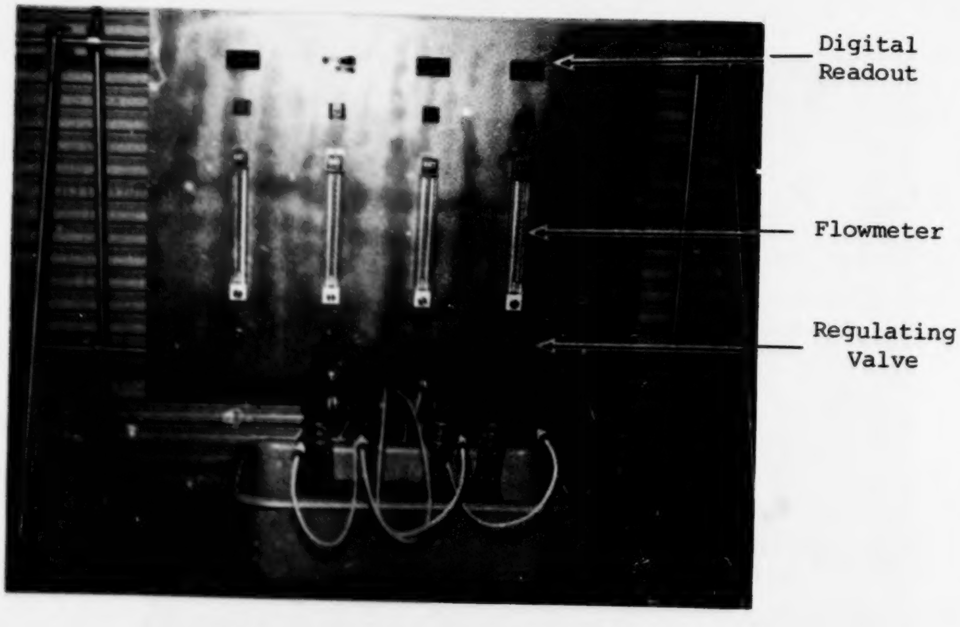

Gas Temperature
Digital Readout
080
Sample
Probe
On-Off
Solenoid
Valve
Flowmeter
Dry
Gas
Meter
Sample
Pump
Drying
Tube
Filter
Impingers
Regulating
Valve
Ice Bath
032
12345
Dilute
Exhaust
Ice Bath
Temperature
Readout
Gas Volume
Digital Readout

Figure 1. SO_2 sample collection flow schematic.



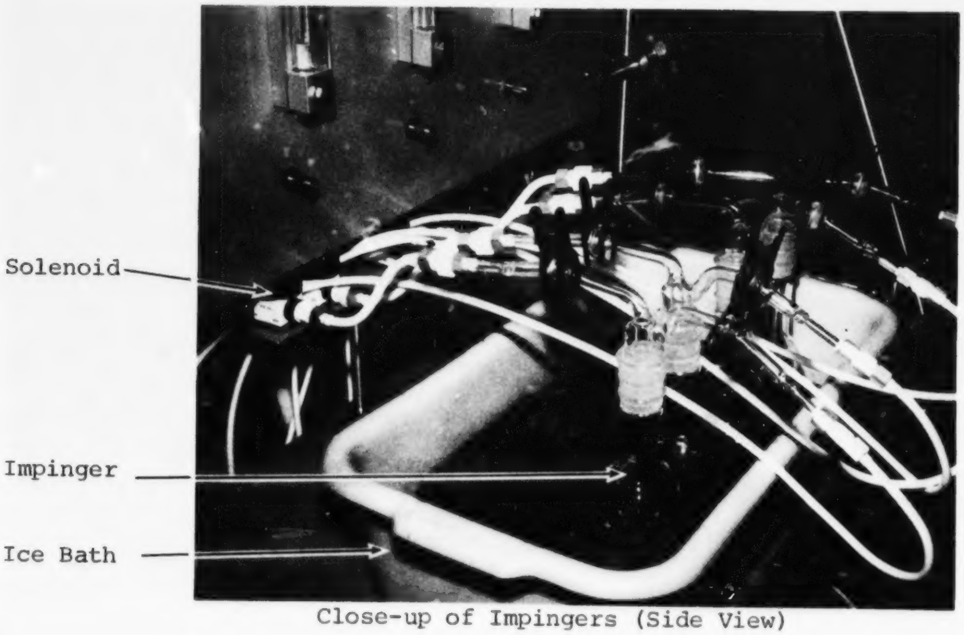
Front View



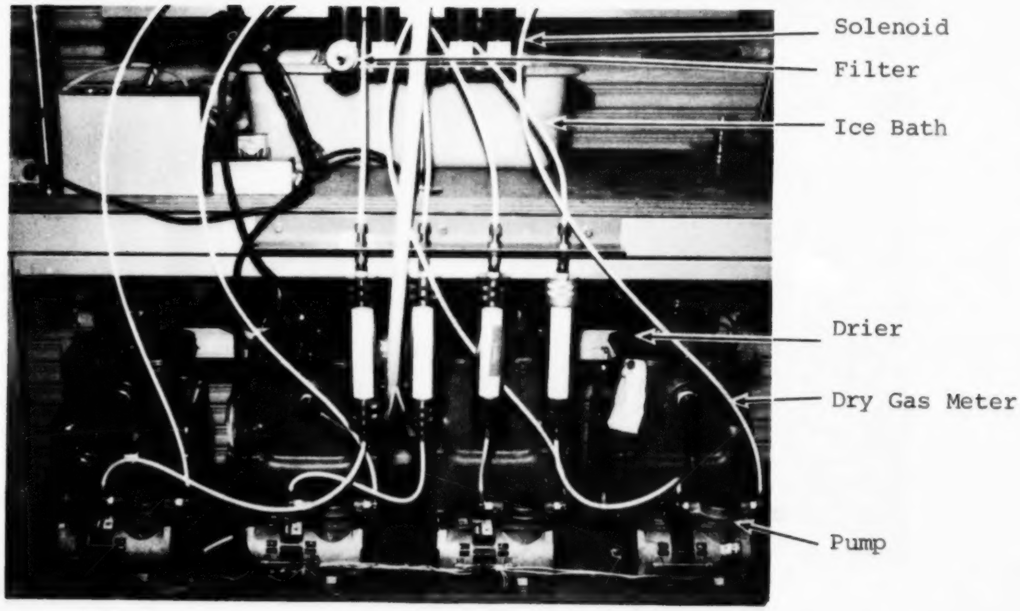
Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. SO_2 sampling system.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). SO_2 sampling system.

bottle and capped. These samples should be analyzed within four or five weeks after collection to prevent sample deterioration. Approximately 2 mℓ of the solution is loaded into the sample loop and injected. This inserts the sample loop volume (0.5 mℓ) of sample into the instrument. An analysis flow schematic and pictures of the ion chromatograph are shown in Figures 3 and 4. The ion chromatograph utilizes two columns, the separator and the suppressor. The 3 × 500 mm analytical column and the 3 × 150 mm precolumn are packed with a patented resin composed of a strong base anion exchanger in the bicarbonate form. The analytical column separates the anions before entering the suppressor column. This 6 × 250 mm glass suppressor column packed with AG 50W-×10, a strong acid cation exchanger neutralized the ionic effect of the eluent while increasing that of the sample ion. The column packing is chosen in the hydrogen form so that in the presence of the eluent ($NaHCO_3$ and Na_2CO_3) H_2CO_3 is generated and when sulfate is introduced H_2SO_4 is formed.

$$NaHCO_3 + \text{Resin-H} \rightleftharpoons \text{Resin-Na} + H_2CO_3$$

$$Na^+\ \text{Anion}^- + \text{Resin-H} \rightleftharpoons \text{Resin-Na} + H^+\ \text{Anion}^-$$

The acid being more conductive than the hydrogen carbonate produces a signal on the conductivity meter. This can be interpreted as peak height from a trace or as peak area measured by the Hewlett-Packard 3354 computer system. Figures 5 and 6 show two representative chromatograms produced in the analysis of a standard and a sample. The ion chromatograph operates at room temperature at a maximum pressure of 500 psi.

CALCULATIONS

This procedure provides a method of determining the concentration of SO_2 in automotive exhaust. When the calculations described below are carried out the concentration is expressed in $\frac{\mu g\ SO_2}{m^3}$ and ppm SO_2. A stepwise derivation of the equation describing the analysis will be provided as well as a copy of the Hewlett-Packard 65 program which includes all calculations. See Figure 7. This program was designed to reduce the amount of time required to do the calculations manually. To illustrate the process two sample calculations will be performed from the information on the data sheet (Figure 8). The first step in the calculations is the assumption that SO_2 is an ideal gas, i.e., the ideal gas law, PV = nrt, is valid. This equation gives the volume of sampled gas corrected to specified temperature and pressure if the experimental conditions are known.

$$V = \frac{PxVx}{Tx+460} \times \frac{Tspec}{Pspec}$$

where V = volume of gas sampled at specified temperature and pressure (ft^3)

Px = experimental pressure (in Hg)

Vx = experimental gas volume collected (ft^3)

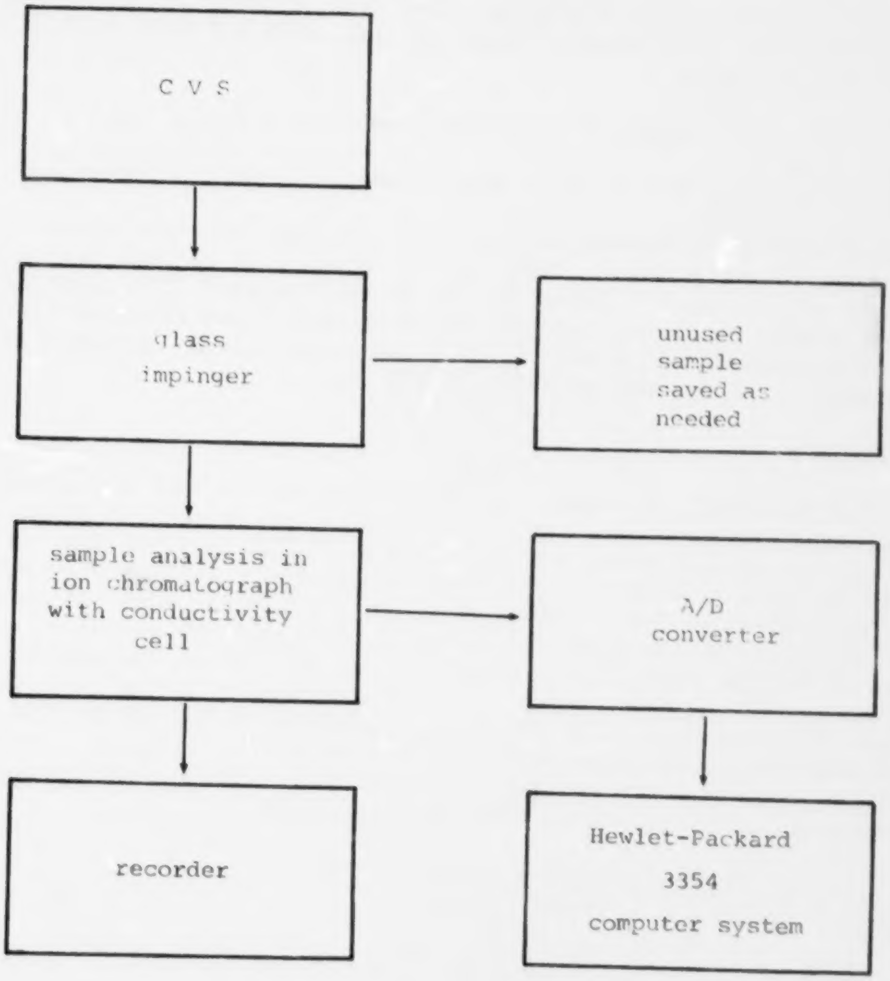

C V S
glass impinger
unused sample saved as needed
sample analysis in ion chromatograph with conductivity cell
A/D converter
recorder
Hewlet-Packard 3354 computer system

Figure 3. SO_2 analysis flow schematic.

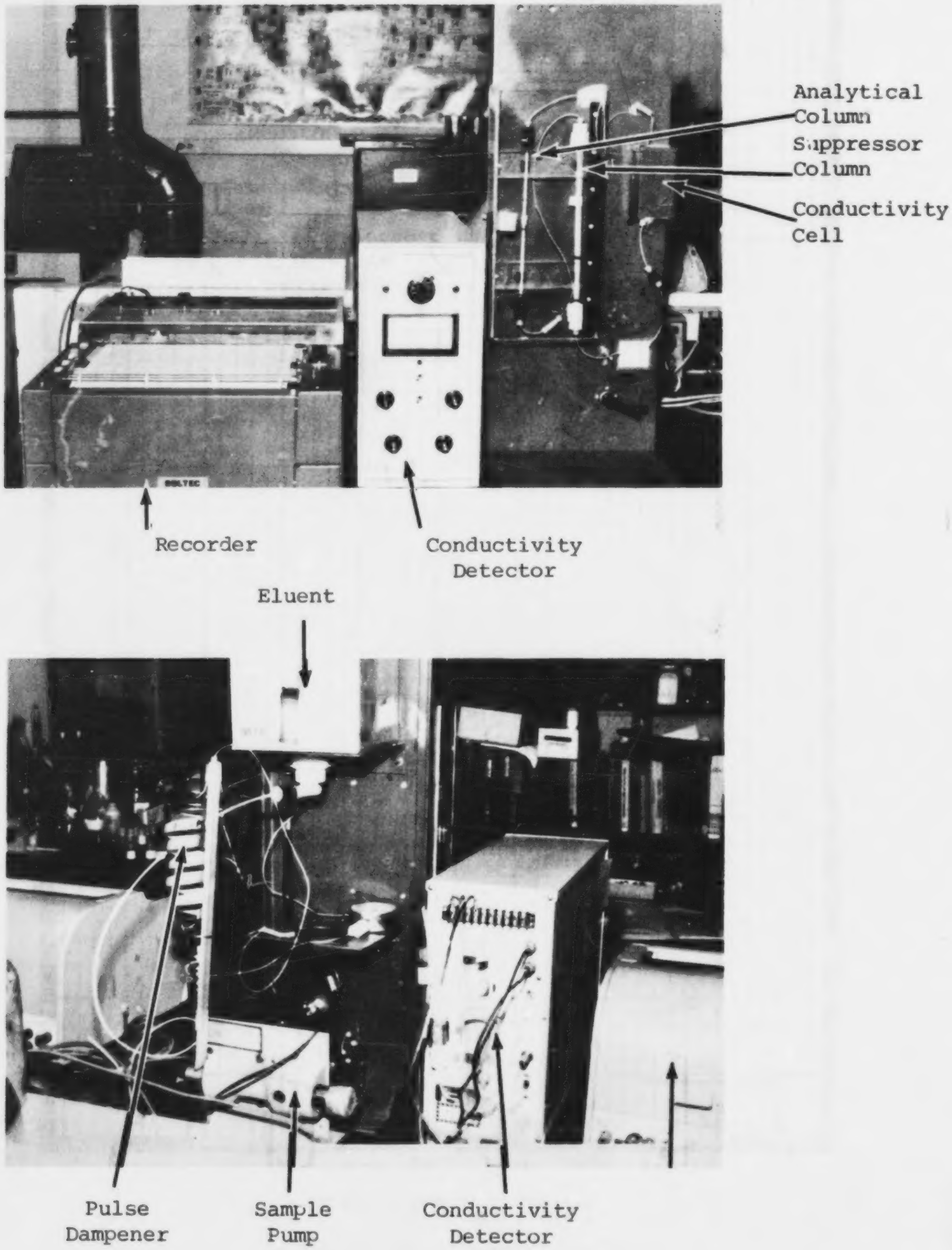
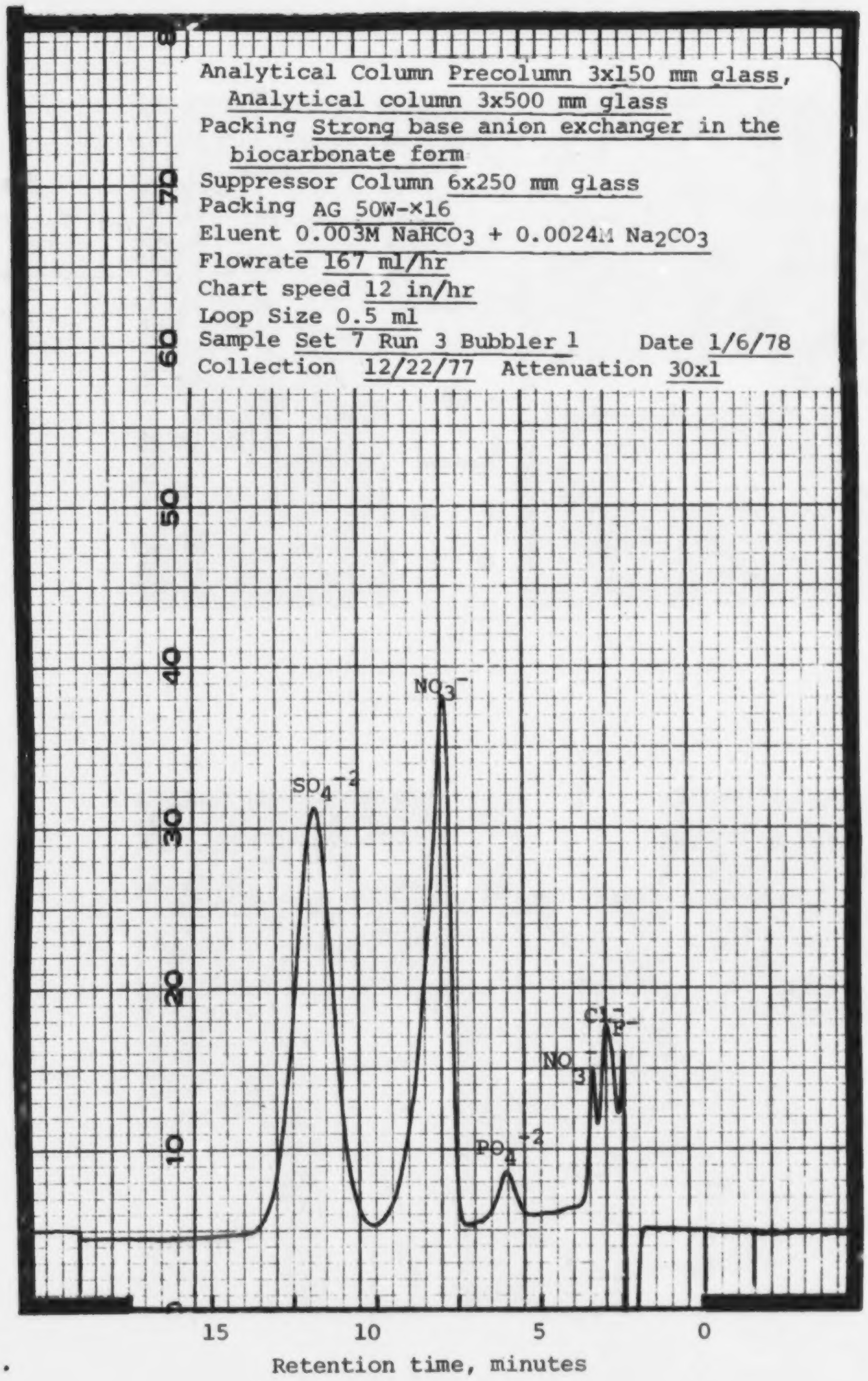
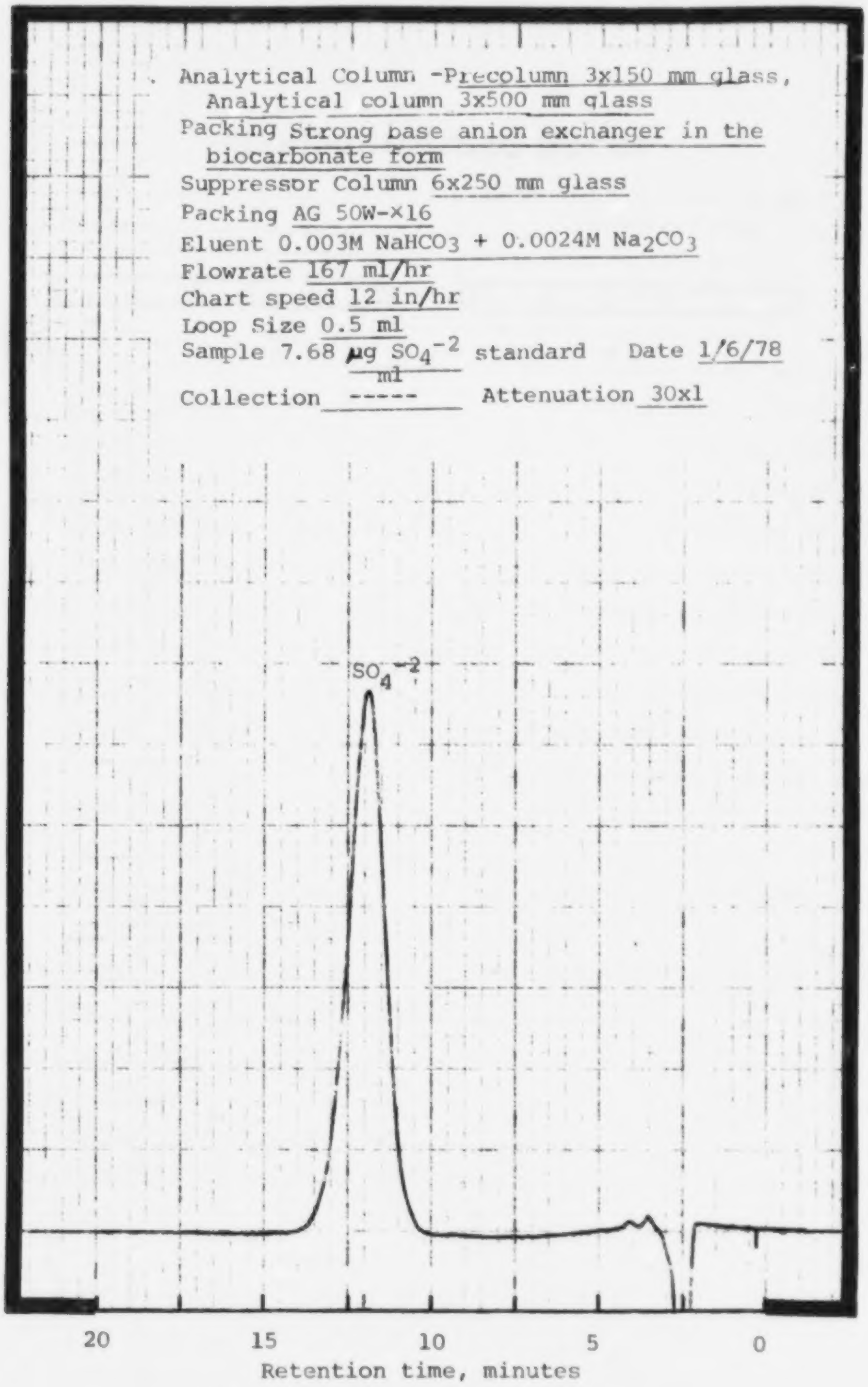

Analytical Column
Suppressor Column
Conductivity Cell
Recorder
Conductivity Detector
Eluent
Pulse Dampener
Sample Pump
Conductivity Detector

Figure 4. SO_2 Ion chromatograph.



Analytical Column Precolumn 3x150 mm glass,
Analytical column 3x500 mm glass
Packing Strong base anion exchanger in the
biocarbonate form
Suppressor Column 6x250 mm glass
Packing AG 50W-×16
Eluent 0.003M $NaHCO_3$ + 0.0024M Na_2CO_3
Flowrate 167 ml/hr
Chart speed 12 in/hr
Loop Size 0.5 ml
Sample Set 7 Run 3 Bubbler 1 Date 1/6/78
Collection 12/22/77 Attenuation 30x1

Figure 5. Sample chromatogram.



Analytical Column -Precolumn 3x150 mm glass,
Analytical column 3x500 mm glass
Packing Strong base anion exchanger in the biocarbonate form
Suppressor Column 6x250 mm glass
Packing AG 50W-×16
Eluent 0.003M $NaHCO_3$ + 0.0024M Na_2CO_3
Flowrate 167 ml/hr
Chart speed 12 in/hr
Loop Size 0.5 ml
Sample 7.68 $\frac{\mu g\ SO_4^{-2}}{ml}$ standard Date 1/6/78
Collection ----- Attenuation 30x1

Figure 6. Standard chromatogram.

HP-65 User Instructions

Title SULFUR DIOXIDE IN EXHAUST (LINEAR) Page ____ of ____

Programmer HARRY E. DIETZMANN Date 11/11/77

STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on; switch to run				
0_2	Feed card in from right to left				
0_3	Initialize		f	REG	
0_4	Set decimal place		DSP	2	
1	Input-sample volume, ft^3		A		
2	Input-Barometric pressure, "Hg		R/S		
3	Input-Sample Temperature, °F		R/S		
4	Input-Dilution factor		R/S		
5	Input-Absorbing reagent volume, ml		R/S		
6	Input-Standard concentration, $\frac{\mu g\ SO_4^{-2}}{ml}$		R/S		
7	Input-Standard area		R/S		
8	Input-Sample Area		R/S		
	Output-Sample concentration, $\frac{\mu g\ SO_2}{m^3}$				
9			R/S		
	Output-Sample concentration, ppm				
			RTN		
			f		
			REG		
			CLX		

Figure 7. HP-65 program form.

HP-65 Program Form

Title SULFUR DIOXIDE IN EXHAUST (LINEAR) Page ____ of ____

SWITCH TO W/PRGM PRESS f PRGM TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS	KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23	Input-Sample vol., ft^3	0		
A	11		0		
3			3		
5			6		
•	83		7		
3			X	71	
1			R/S	84	
÷	81		RTN		
5					
2					
8					
X	71				
2					
9					
•	83				
9					
2					
÷	81				
R/S	84	Input-barometer, "Hg			
X	71				
STO 1	33 01				
R/S	84	Input-sample temp., °F			
4					
6					
0					
+	61				
RCL 1	34 01				
g x⇄y					
÷					
g 1/x	35 04				
R/S	84	Input-dilution factor			
X	71				
R/S	84	Input-Abs.soln.vol., ml			
X	71				
R/S	84	Input-Stand.Conc. $\frac{\mu g\ SO_4^{-2}}{ml}$			
X	71				
R/S	84	Input-Standard Area			
÷	81				
R/S	84	Input-Sample Area			
X	71				
0					
•	83				
6					
6					
7					
X	71				
R/S	84				
0					
•	83				
0					

REGISTERS

R_1 ____

R_2 ____

R_3 ____

R_4 ____

R_5 ____

R_6 ____

R_7 ____

R_8 ____

R_9 ____

LABELS

A ____
B ____
C ____
D ____
E ____
0 ____
1 ____
2 ____
3 ____
4 ____
5 ____
6 ____
7 ____
8 ____
9 ____

FLAGS

1 ____

2 ____

9320-0616

TO RECORD PROGRAM INSERT MAGNETIC CARD WITH SWITCH SET AT W PRGM

Figure 7 (Cont'd.) HP-65 program form.

SWRI PROJECT NO. ______________ TEST NO. 001 TEST DATE: 12-12-77 VEHICLE: PRACTICE
FUEL: EM-237-001 CVS NO. 3 TUNNEL SIZE 8 in DRIVER: Bill P MILES: 1000
SAMPLE COLLECTION BY: MaryAnn P. CHEMICAL ANALYSIS BY: MaryAnn P. CALCULATIONS BY: MaryAnn P.
GENERAL COMMENTS: ______________

NO.	DRIVING CYCLE	SAMPLING CONDITIONS			DILUTION FACTOR	ABSORB. REAGENT VOLUME ML	STANDARD		SAMPLE			
		VOLUME FT^3	B.P. "HG	TEMP. °F			ug NH_4^+/ml	AREA	AREA	ug NH_3/m^3	PPM	
1	FTP-1	1.189	29.47	74.7	1	25	10	3200	4000	6360	2.34	
2	FTP-2	2.040	29.48	75.0	1	25	30	4500	3500	6930	2.54	
3	FTP-3	1.250	29.49	74.5	1	25	10	3200	4300	6500	2.39	
4	SET-7	3.240	29.50	75.0	1	25	40	4200	4500	8000	2.94	
5	HFET	1.690	29.50	74.7	1	25	20	5700	5500	6670	2.45	
6	NYCC	1.410	29.51	74.9	1	25	15	4900	5000	6630	2.43	
7												
8	BG	2.000	29.45	74.9	1	25	1.0	3000	2700	273	0.10	
☒	☒	①	②	③	④	⑤	⑥	⑦	⑧			

Figure 8. SO_2 data sheet.

Tx = experimental temperature (°F)

Tspec = specified temperature = 68°F = 528°R

Pspec = specified pressure = 29.92 in Hg

Next, the quantity of SO_2 in this volume of gas is calculated. The ion chromatograph measures the amount of sulfate (from SO_2) in $\frac{\mu g\ SO_4^{-2}}{m\ell}$. Assuming linearity between concentration of sulfate and peak area, a standard of known sulfate concentration is compared to a bubbled exhaust sample.

$$\frac{Cst}{AREAst} = \frac{Csamp}{AREAsamp}$$

$$\therefore \quad Csamp = \frac{Cst \times AREAsamp}{AREAst}$$

where Csamp = concentration of SO_4^{-2} in sample $\frac{\mu g\ SO_4^{-2}}{m\ell}$

Cst = concentration of SO_4^{-2} in standard $\frac{\mu g\ SO_4^{-2}}{m\ell}$

AREAsamp = area of sample (relative units)

AREAst = area of standard (relative units)

Converting to $\mu g\ SO_2/m\ell$:

$$Csamp \times \frac{64.06\ g/mole\ SO_2}{96.06\ g/mole\ SO_4^{-2}} = 0.667\ Csamp$$

If the sample has been diluted the dilution factor, DF, needs to be included

$$0.667\ Csamp \times DF$$

This represent the amount of SO_2 in one mℓ of absorbing solution. The volume of absorbing solution is multiplied by this last quantity to give the amount of SO_2 collected.

$$0.667\ Csamp \times DF \times \text{absorb. vol. } (m\ell) = \mu g\ SO_2$$

The concentration of SO_2 in $\frac{\mu g\ SO_2}{m^3}$ in the exhaust sample is obtained by dividing $\mu g\ SO_2$ by gas volume (corrected from ft^3 to m^3).

Concentration of SO_2, $\frac{\mu g\ SO_2}{m^3}$ =

$$\frac{0.667\ \frac{\mu g\ SO_2}{\mu g\ SO_4^{-2}} \times \frac{\text{Cst, } \frac{\mu g\ SO_4^{-2}}{m\ell} \times \text{AREAsamp}}{\text{AREAst}} \times \text{DF} \times \text{absorb. vol., } m\ell}{\frac{\text{Px, in Hg} \times \text{Vx, ft}^3}{\text{Tx, °F} + 460} \times \frac{528\text{°R}}{29.92 \text{ in Hg}}}$$

$$= \frac{0.667\ \frac{\mu g\ SO_2}{\mu g\ SO_4^{-2}} \times \text{Cst, } \frac{\mu g\ SO_4^{-2}}{m\ell} \times \text{AREAsamp} \times \text{DF} \times \text{absorb. vol., } m\ell}{\text{Px, in Hg} \times \text{Vx, ft}^3} \times$$

$$\frac{(\text{Tx, °F} + 460) \times 29.92 \text{ in Hg} \times 35.31\ \frac{m^3}{ft^3}}{528\text{°R} \times \text{AREAst}}$$

To find the SO_2 concentration in ppm the density of the gas at the specified conditions is needed. The density of SO_2 at 0°C and 29.92 in Hg is 2.927 g/lit. This can be corrected to 68 F (20°C = 293°K) and 29.92 in Hg using Charles' version of the ideal gas law:

$$\frac{V}{T} = \frac{V_1}{T_1}$$

where V_1 is the volume at 0°C (lit) = 1.0 lit
T_1 is 0°C = 273°K
V is the volume at 20°C (lit)
T is 20°C = 293°K

$$V = \frac{(1.0 \text{ lit})\ (293\text{°K})}{273\text{°K}} = 1.073 \text{ lit}$$

Density at 68°F (20°C) and 29.92" Hg = $\frac{2.927g}{1.073 \text{ lit}}$

$$= 2.728 \text{ g/lit} = 2728\ \frac{\mu g}{m\ell}$$

$$= 0.000367\ \frac{m\ell}{\mu g}$$

$$\frac{\mu g\ SO_2}{m^3} \times 0.000367\ \frac{m\ell}{\mu g} = \frac{m\ell}{m^3} = \text{ppm } SO_2$$

Sample Calculation

Example 1

Assume 1.189 ft^3 of exhaust was collected in 25 mℓ of 3 percent H_2O_2 in the FTP-1 driving cycle at a barometric pressure of 29.47 in Hg (corrected) and temperature of 74.7°F. The sampling and analysis were both performed according to the procedure outlined in a previous section. An excess of sample injected into the 0.5 mℓ sample loop produced a peak area of 4000 counts and the corresponding standard, $\frac{10\ \mu g\ SO_4^{-2}}{m\ell}$, an area of 3200 counts.

$$\text{ppm } SO_2 = \frac{0.000367 \frac{m\ell}{\mu g\ SO_2} \times 0.667 \frac{\mu g\ SO_2}{\mu g\ SO_4^{-2}} \times \text{Cst}, \frac{\mu g\ SO_4^{-2}}{m\ell} \times \text{AREAsamp}}{\text{Px, in Hg} \times \text{Vx}, ft^3} \times$$

$$\frac{\text{DF} \times \text{absorb. vol., } m\ell \times (\text{Tx, }°F + 460) \times 29.92 \text{ in Hg} \times 35.31 \frac{m^3}{ft^3}}{528°R \times \text{AREAst}}$$

$$= \frac{0.000367 \times 0.667 \times 10 \times 4000 \times 1 \times 25 \times (74.7 + 460) \times 29.92 \times 35.31}{29.47 \times 1.189 \times 528 \times 3200}$$

Sample ppm SO_2 = 2.34 ppm

Example 2

Assume that in the SET-7 driving cycle dilute automotive exhaust was collected in 25 mℓ of 3 percent H_2O_2 according to the procedure described previously. The sampling conditions under which the 3.240 ft^3 of exhaust was collected were 75.0°F and 29.50 in Hg. 4200 counts was the area produced by the 40 $\frac{\mu g\ SO_4^{-2}}{m\ell}$ standard and the exhaust sample yielded an area of 4500 counts. Inserting these values into the same equation used in Example 1 gives a concentration of 2.94 ppm SO_2. Note that the information from the data sheet used in these calculations does not necessarily represent actual values obtained from exhaust sampling.

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APPENDIX E

NITROUS OXIDE PROCEDURE

THE MEASUREMENT OF NITROUS OXIDE IN EXHAUST

This procedure was developed to measure nitrous oxide (N_2O) in dilute gasoline and diesel exhaust. Standard CVS bag samples are analyzed for N_2O using calibration blends to quantify the results. Gas chromatograph peak areas are obtained using a Hewlett-Packard 3354 computer system. This technique has a minimum detection limit of less than 0.01 ppm. The total system schematic for the analysis of N_2O in exhaust is shown in Figure 1.

ANALYTICAL SYSTEM

The analysis for N_2O in exhaust is conducted with a gas chromatograph system using a Perkin-Elmer Model 3920B electron capture detector. The system employs two pneumatically operated electrically controlled Seiscor valves, an analytical column, and a stripper column. The gas chromatograph separation is obtained at room temperature. A special control console was fabricated to house the entire system except for the electron capture detector.

A stripper column is included as a precautionary measure to prevent unwanted heavier molecular weight exhaust species from the analytical system from entering. Figure 2 (Step 1) illustrates the gas chromatograph flow schematic with the gas sampling valve in the purge position and the backflush valve is foreflushing to the analytical column. Figure 3 (Step 2) illustrates the flow schematic when the gas sampling valve is actuated and the backflush valve still in the foreflush position to the analytical column. Once the N_2O peak foreflushing has eluted, the backflush valve is activated and the heavier molecular weight species retained on the stripper column are backflushed to vent, as shown in Figure 4. A summary of the individual steps is presented below:

	Gas Sampling Valve		Backflush Valve	
Step	Position	Function	Position	Function
1	off	purge GSV w/sample	off	foreflush to analytical column
2	on	sample injected	off	foreflush to analytical column
3	on	sample injected	on	backflush to vent

Under normal conditions, it is not necessary to backflush the calibration standards since they are free of contaminants that would interfere

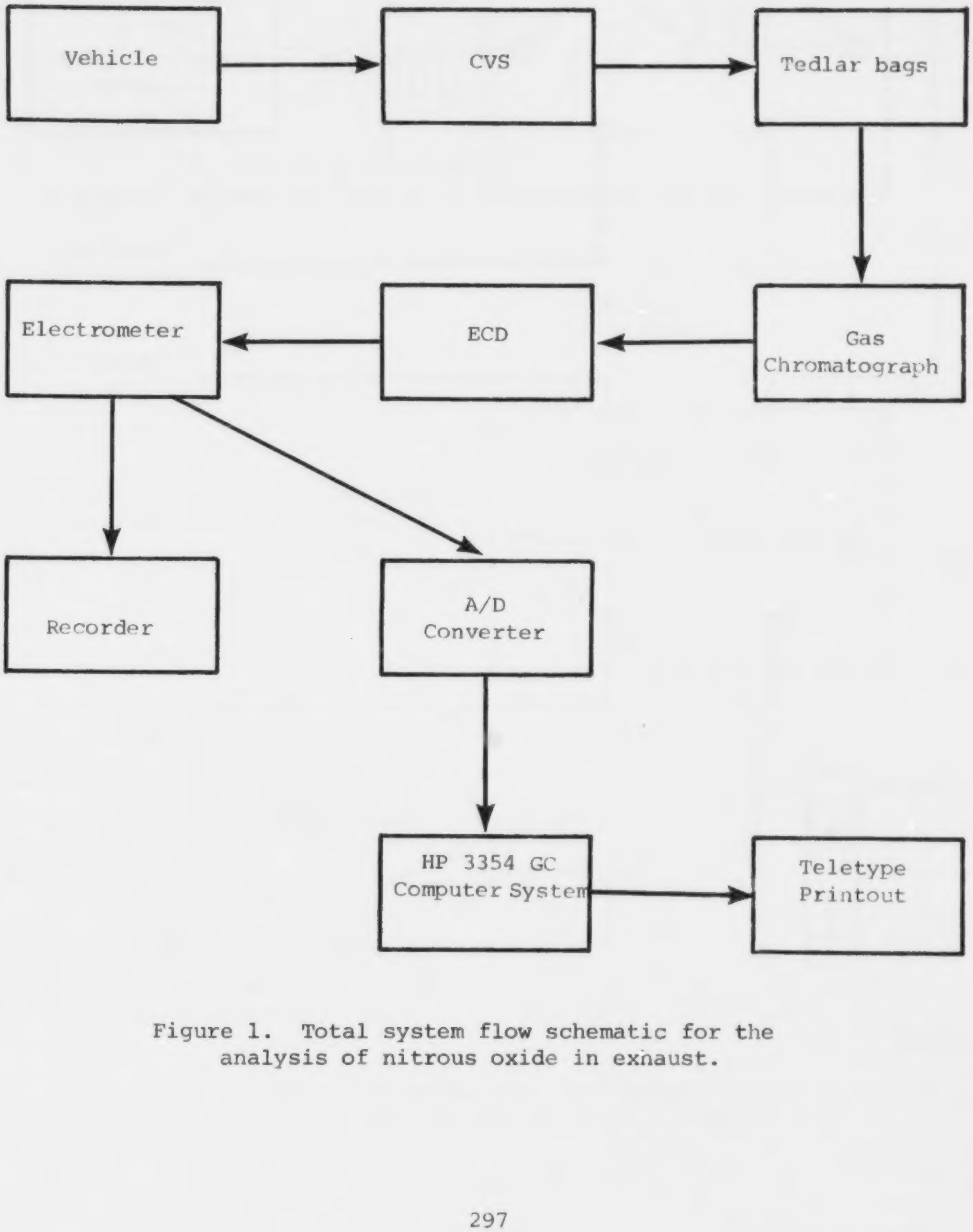

Vehicle
CVS
Tedlar bags
Gas Chromatograph
ECD
Electrometer
Recorder
A/D Converter
HP 3354 GC Computer System
Teletype Printout

Figure 1. Total system flow schematic for the analysis of nitrous oxide in exhaust.

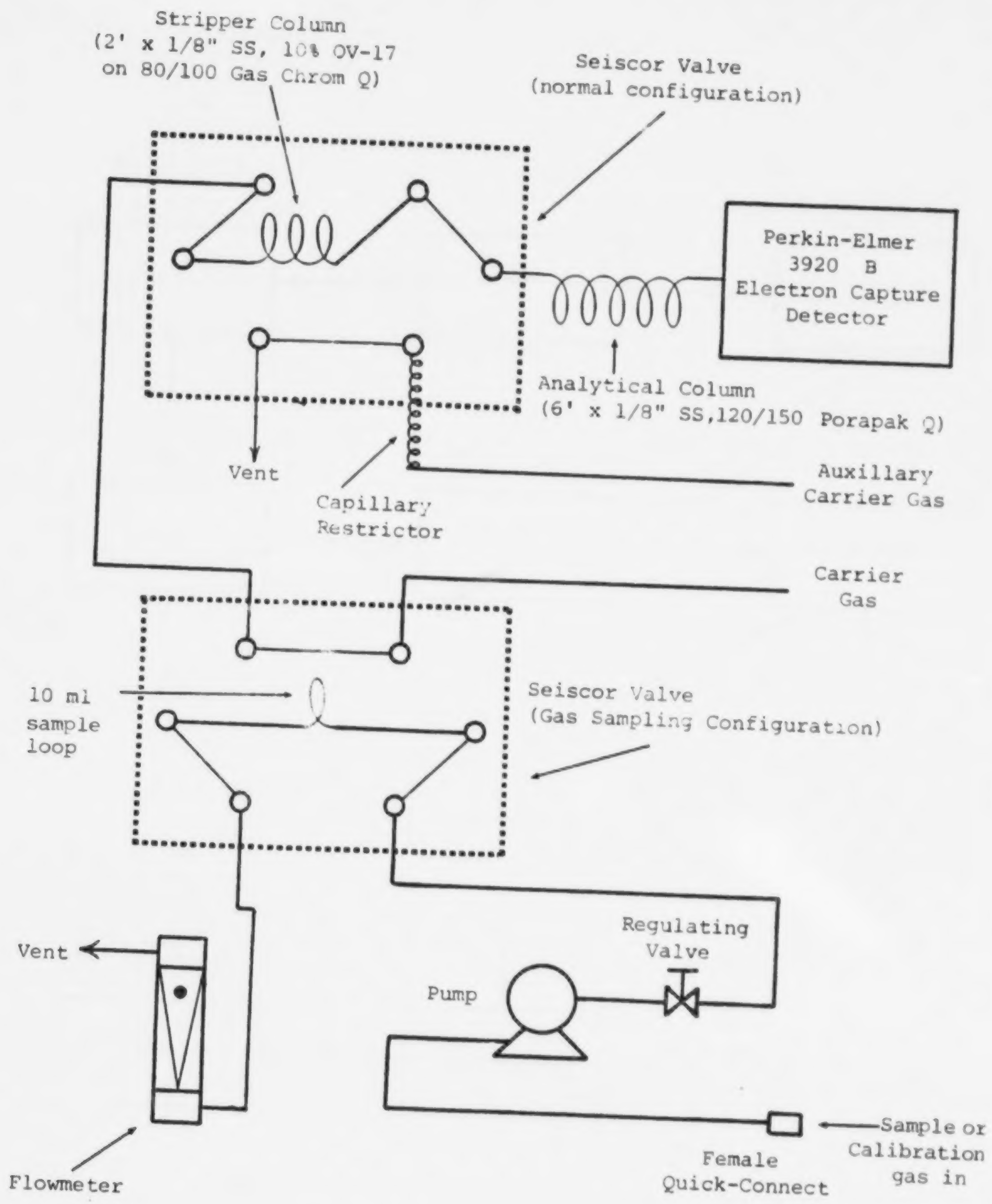

Stripper Column
(2' x 1/8" SS, 10% OV-17
on 80/100 Gas Chrom Q)
Seiscor Valve
(normal configuration)
Perkin-Elmer
3920 B
Electron Capture
Detector
Analytical Column
(6' x 1/8" SS,120/150 Porapak Q)
Vent
Capillary
Restrictor
Auxillary
Carrier Gas
Carrier
Gas
10 ml
sample
loop
Seiscor Valve
(Gas Sampling Configuration)
Vent
Regulating
Valve
Pump
Flowmeter
Female
Quick-Connect
Sample or
Calibration
gas in

Figure 2. Flow schematic of nitrous oxide analytical system (Step 1 - Purge of sample loop of GSV).

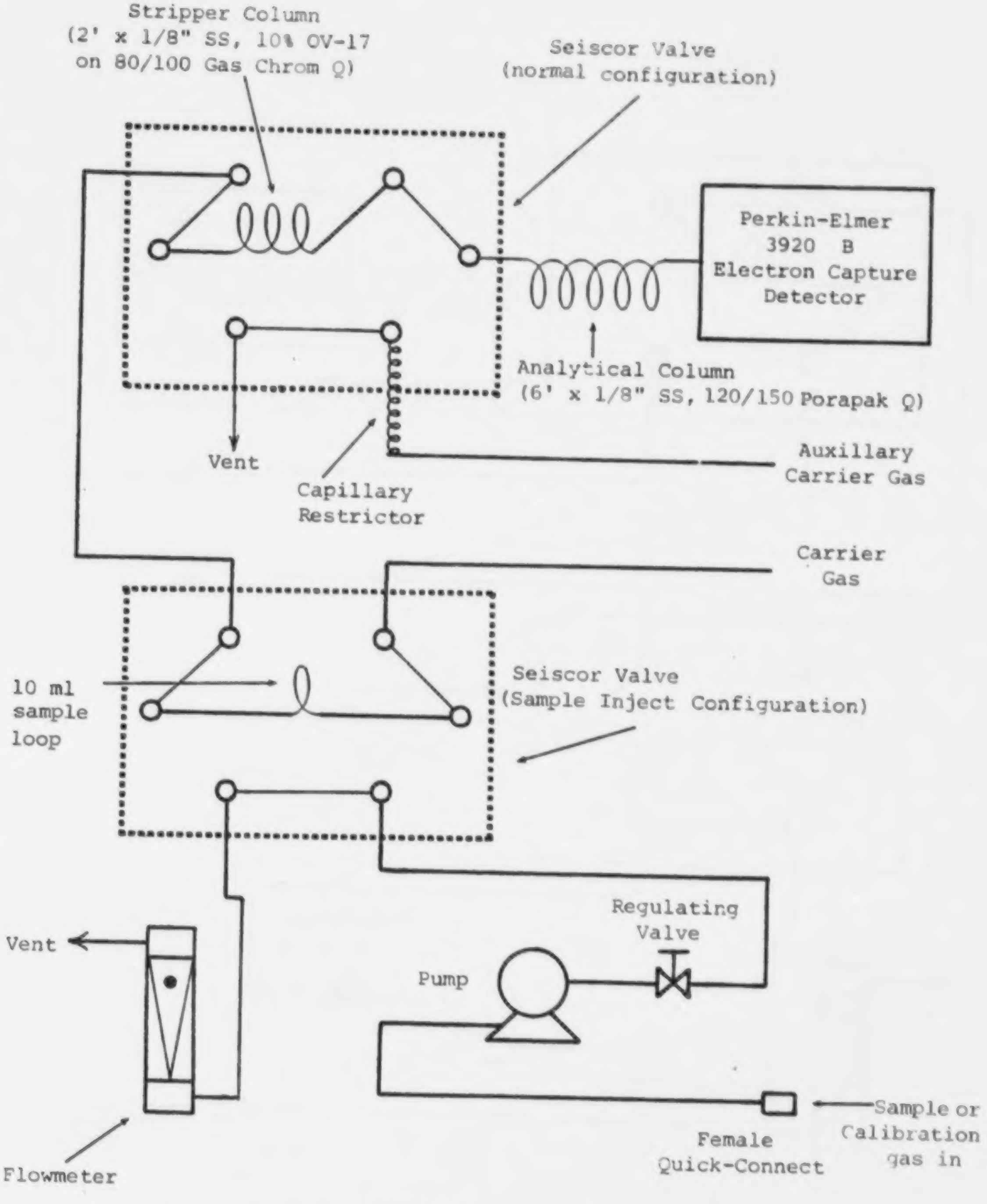

Stripper Column
(2' x 1/8" SS, 10% OV-17
on 80/100 Gas Chrom Q)
Seiscor Valve
(normal configuration)
Perkin-Elmer
3920 B
Electron Capture
Detector
Analytical Column
(6' x 1/8" SS, 120/150 Porapak Q)
Vent
Capillary
Restrictor
Auxillary
Carrier Gas
Carrier
Gas
10 ml
sample
loop
Seiscor Valve
(Sample Inject Configuration)
Regulating
Valve
Vent
Pump
Flowmeter
Female
Quick-Connect
Sample or
Calibration
gas in

Figure 3. Flow schematic of nitrous oxide analytical system (Step 2 - Inject sample or calibration gas into system).

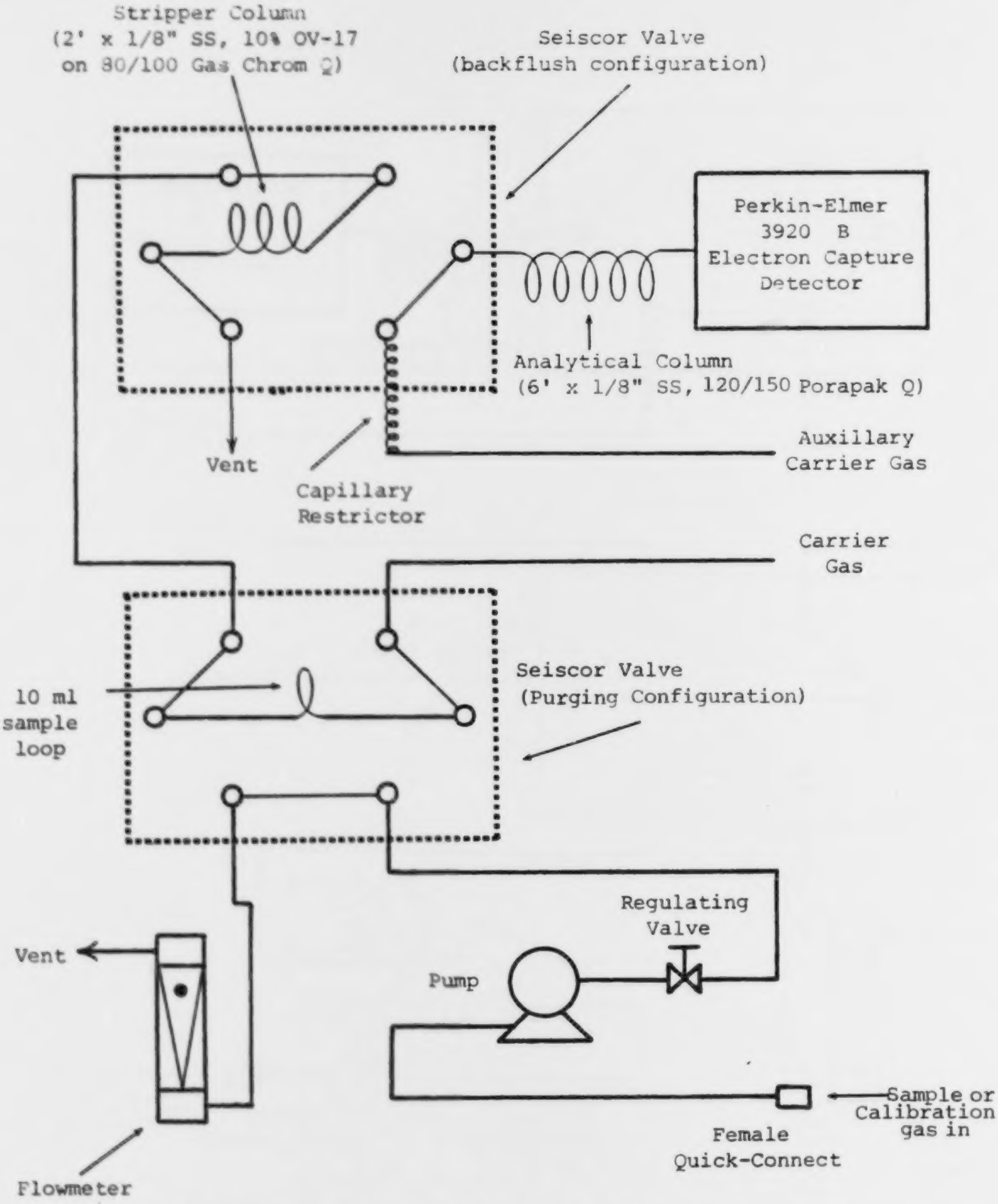

Stripper Column
(2' x 1/8" SS, 10% OV-17
on 80/100 Gas Chrom Q)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920 B
Electron Capture
Detector
Analytical Column
(6' x 1/8" SS, 120/150 Porapak Q)
Auxiliary
Carrier Gas
Vent
Capillary
Restrictor
Carrier
Gas
10 ml
sample
loop
Seiscor Valve
(Purging Configuration)
Regulating
Valve
Vent
Pump
Sample or
Calibration
gas in
Female
Quick-Connect
Flowmeter

Figure 4. Flow schematic of nitrous oxide analysis system (Step 3 - Backflush OV-17 stripper column).

with tha analytical column. A typical gas chromatograph trace for a calibration blend is shown if Figure 5. A baseline separation is obtained and the N_2O peak area is obtained using a Hewlett-Packard 3354 GC computer system.

On gasoline and diesel samples it is necessary that the backflush is included in the analysis to prevent contamination of the analytical column. Using the system described, 60 seconds are allocated to the foreflush position and 360 seconds are allowed for backflushing the stripper column. A typical gasoline-CVS sample GC trace is presented in Figure 6, while a diesel CVS-sample gas chromatograph trace is illustrated in Figure 7. The gas chromatograph operating conditions are listed on Figures 6 and 7.

CONTROL SYSTEM

The control of the two Seiscor valves is accomplished by ATC timers and ASCO electric solenoid valves. The electrical schematic for the control of the Seiscor valves using these timers and electric solenoid valves is shown in Figure 8. The flow schematic for vacuum and pressure lines to the Seiscor valve are presented in Figures 9-11.

EQUIPMENT

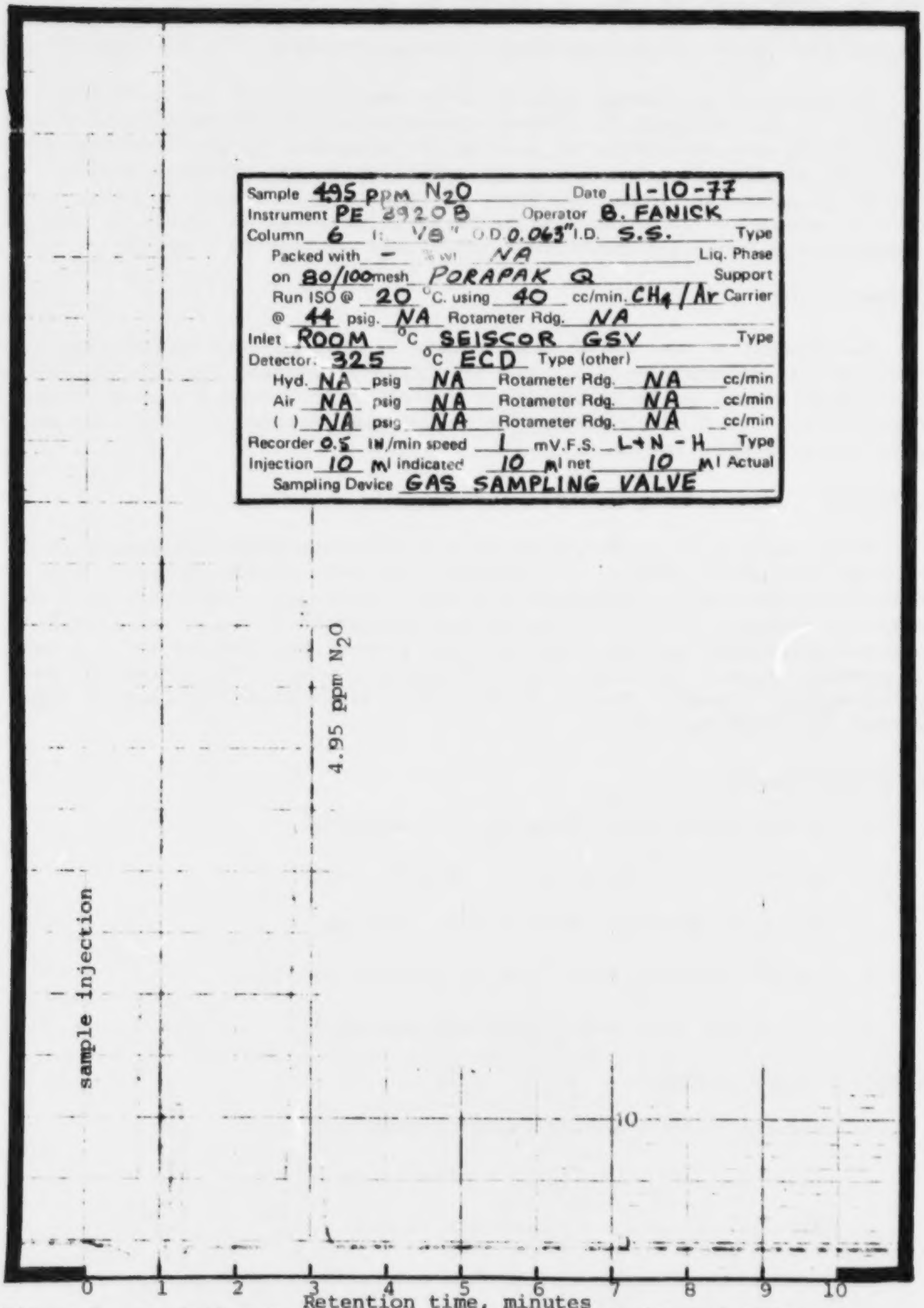
This analysis is performed using a gas chromatograph equipped with an electron capture detector. The detector, detector heater controls, electrometer, recorder and GC integrator are major electronic components in the detection system. A control console was fabricated to house the mechanical hardware items that are necessary for the proper operation of the N_2O analysis system. Figure 12 illustrates the complete analytical system for measuring N_2O in exhaust. The major items that are included in each of these systems is listed below:

Gas Chromatograph

1. Perkin-Elmer Model 3920B gas chromatograph
2. Linearized electron capture detector (ECD)
3. Leeds and Northrup Model W 1 mv recorder
4. Hewlett-Packard Model 3354 GC computer system
5. Hewlett-Packard Model 1865A A/D converter

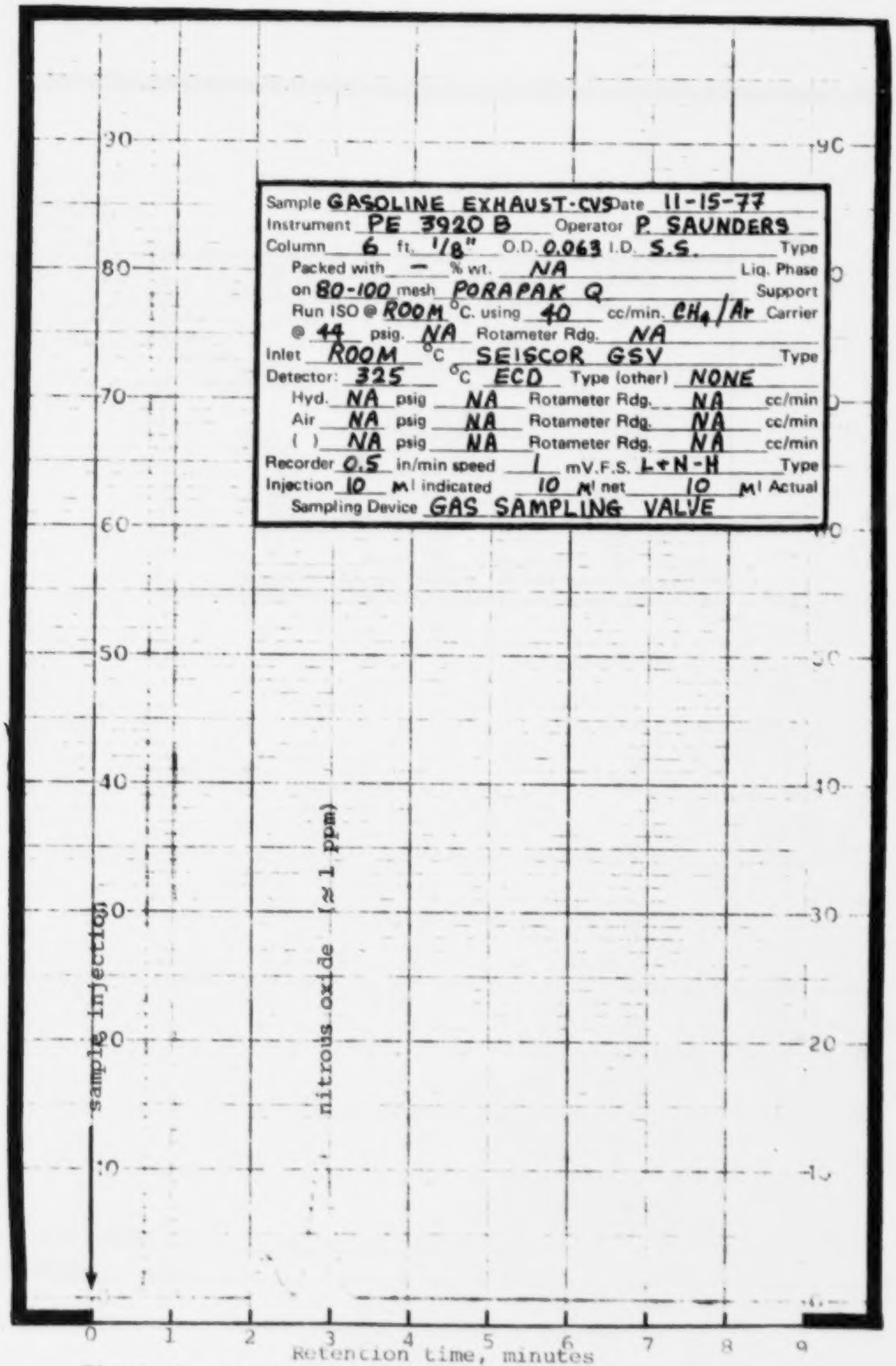
Control Console System

1. Seiscor valve - gas sampling configuration
2. Seiscor valve - backflush configuration
3. ATC timers, Model 325A346A10PX (2 ea)
4. Analytical column, 6' x 1/8" SS, 120/150 Poropak Q



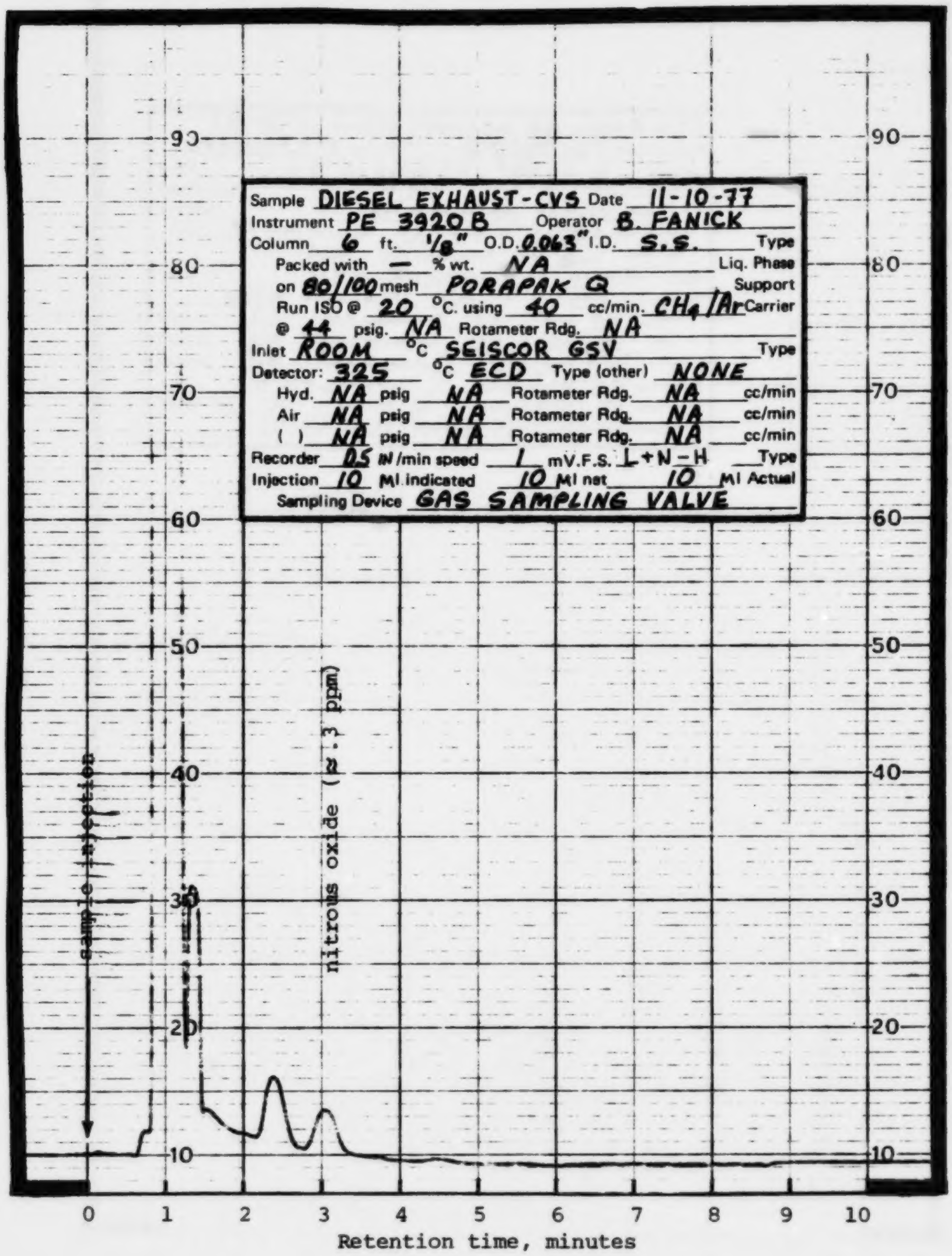
Sample 495 ppm N_2O Date 11-10-77
Instrument PE 3920B Operator B. FANICK
Column 6 ft. 1/8" O.D. 0.063" I.D. S.S. Type
Packed with – % wt NA Liq. Phase
on 80/100 mesh PORAPAK Q Support
Run ISO @ 20 °C. using 40 cc/min. CH_4/Ar Carrier
@ 44 psig. NA Rotameter Rdg. NA
Inlet ROOM °C SEISCOR GSV Type
Detector. 325 °C ECD Type (other)
Hyd. NA psig NA Rotameter Rdg. NA cc/min
Air NA psig NA Rotameter Rdg. NA cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 0.5 in/min speed 1 mV.F.S. L+N - H Type
Injection 10 ml indicated 10 ml net 10 ml Actual
Sampling Device GAS SAMPLING VALVE

Figure 5. Typical N_2O calibration blend gas chromatograph trace.



Sample GASOLINE EXHAUST-CVS Date 11-15-77
Instrument PE 3920 B Operator P. SAUNDERS
Column 6 ft. 1/8" O.D. 0.063 I.D. S.S. Type
Packed with — % wt. NA Liq. Phase
on 80-100 mesh PORAPAK Q Support
Run ISO @ ROOM °C. using 40 cc/min. CH_4/Ar Carrier
@ 44 psig. NA Rotameter Rdg. NA
Inlet ROOM °C SEISCOR GSV Type
Detector: 325 °C ECD Type (other) NONE
Hyd. NA psig NA Rotameter Rdg. NA cc/min
Air NA psig NA Rotameter Rdg. NA cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 0.5 in/min speed 1 mV.F.S. L+N-H Type
Injection 10 μl indicated 10 μl net 10 μl Actual
Sampling Device GAS SAMPLING VALVE

Figure 6. Typical gasoline-CVS exhaust sample.



Sample DIESEL EXHAUST-CVS Date 11-10-77
Instrument PE 3920 B Operator B. FANICK
Column 6 ft. 1/8" O.D. 0.063" I.D. S.S. Type
Packed with — % wt. NA Liq. Phase
on 80/100 mesh PORAPAK Q Support
Run ISO @ 20 °C. using 40 cc/min. CH_4/Ar Carrier
@ 44 psig. NA Rotameter Rdg. NA
Inlet ROOM °C SEISCOR GSV Type
Detector: 325 °C ECD Type (other) NONE
Hyd. NA psig NA Rotameter Rdg. NA cc/min
Air NA psig NA Rotameter Rdg. NA cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 0.5 IN /min speed 1 mV.F.S. L+N-H Type
Injection 10 Ml indicated 10 Ml net 10 Ml Actual
Sampling Device GAS SAMPLING VALVE

90
80
70
60
50
40
30
20
10
sample injection
nitrous oxide (≈ .3 ppm)
0
1
2
3
4
5
6
7
8
9
10
Retention time, minutes

Figure 7. Typical diesel-CVS exhaust sample.

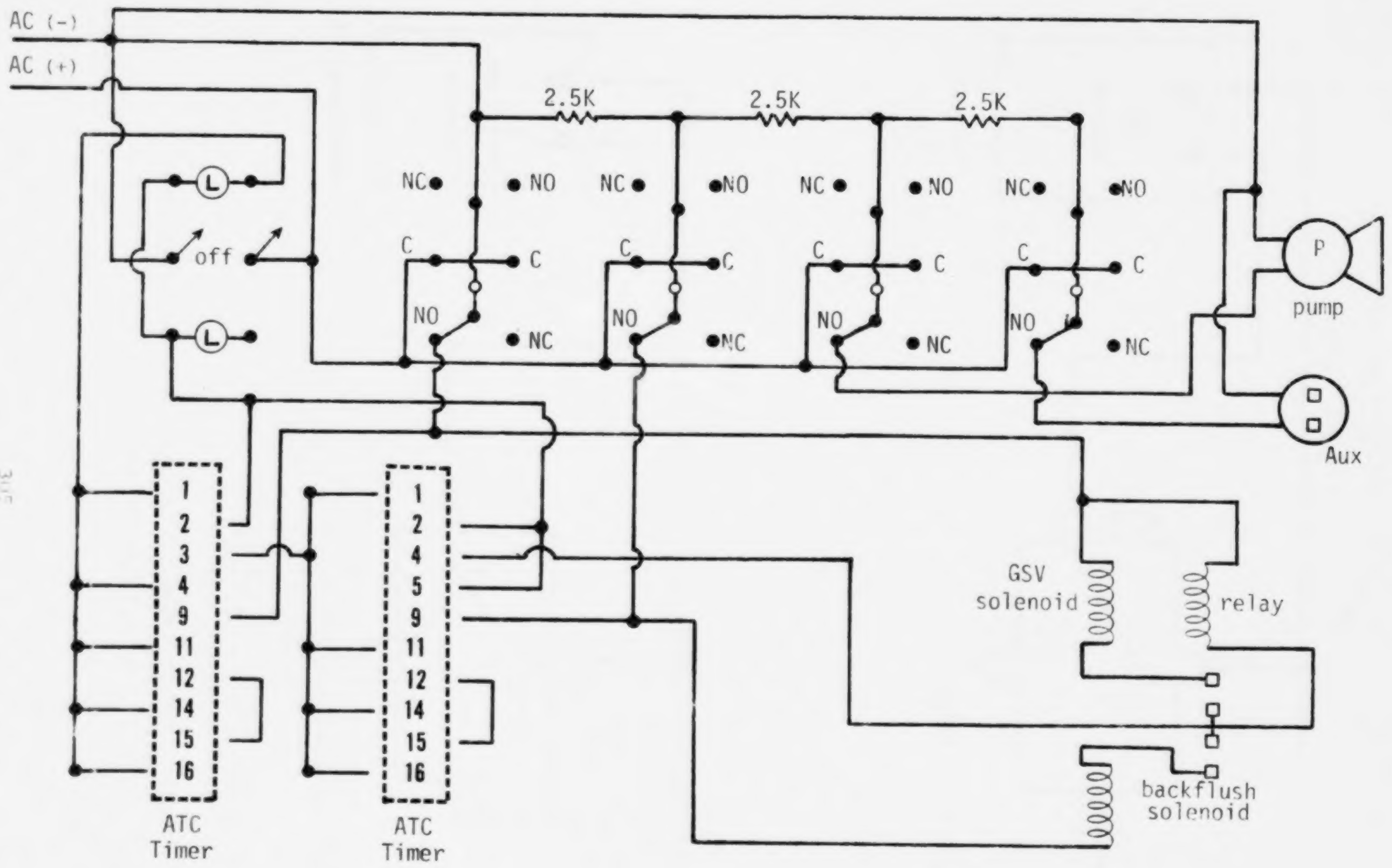

AC (-)
AC (+)
off
L
L
2.5K
2.5K
2.5K
NC
NO
C
C
NO
NC
P
pump
Aux
GSV solenoid
relay
backflush solenoid
1
2
3
4
9
11
12
14
15
16
ATC Timer
1
2
4
5
9
11
12
14
15
16
ATC Timer

Figure 8. Electrical schematic for nitrous oxide analysis system.

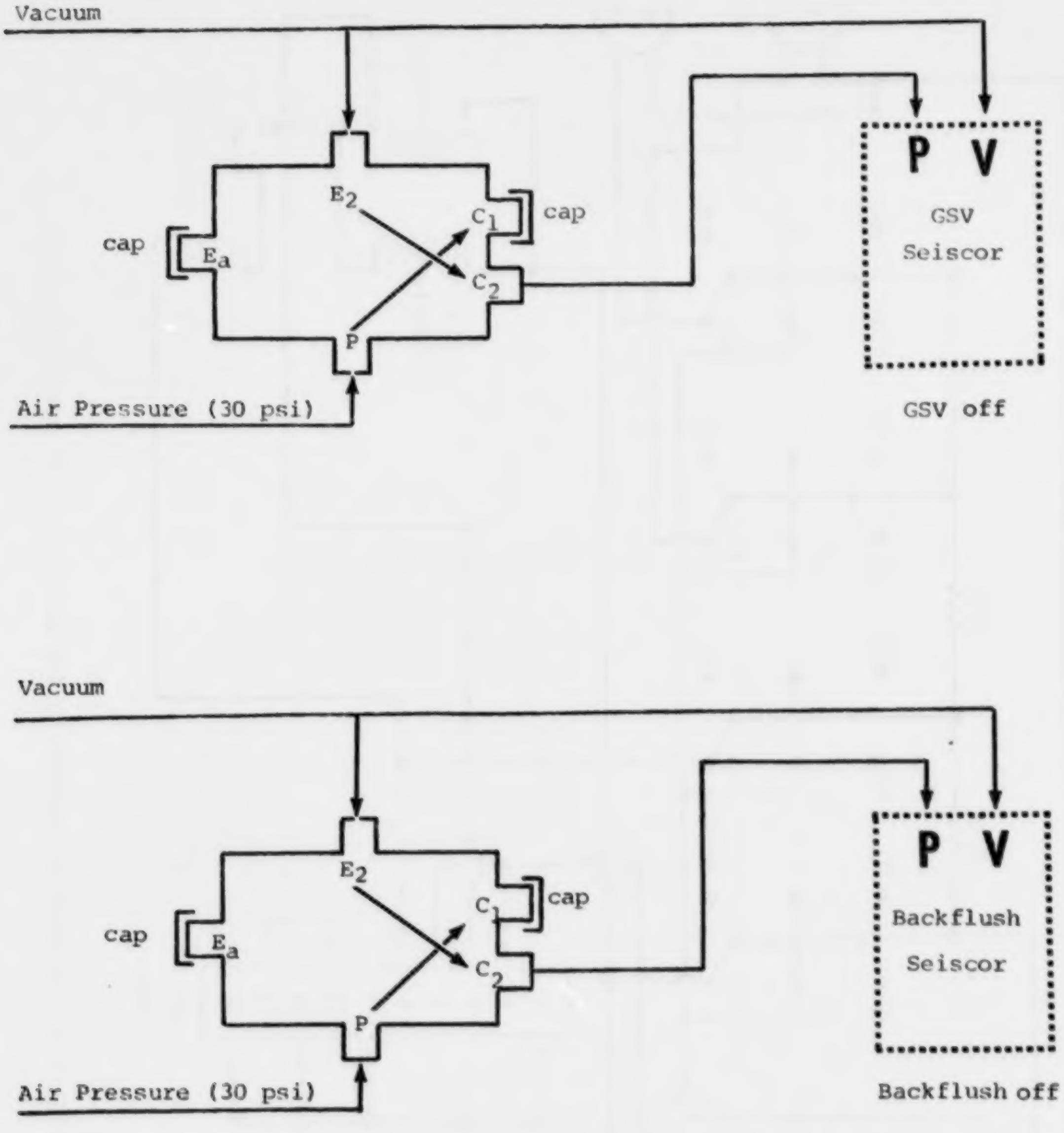

Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
GSV
Seiscor
GSV off
Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
Backflush
Seiscor
Backflush off

Figure 9. Flow schematic in electric solenoid valves (Both valves de-energized).

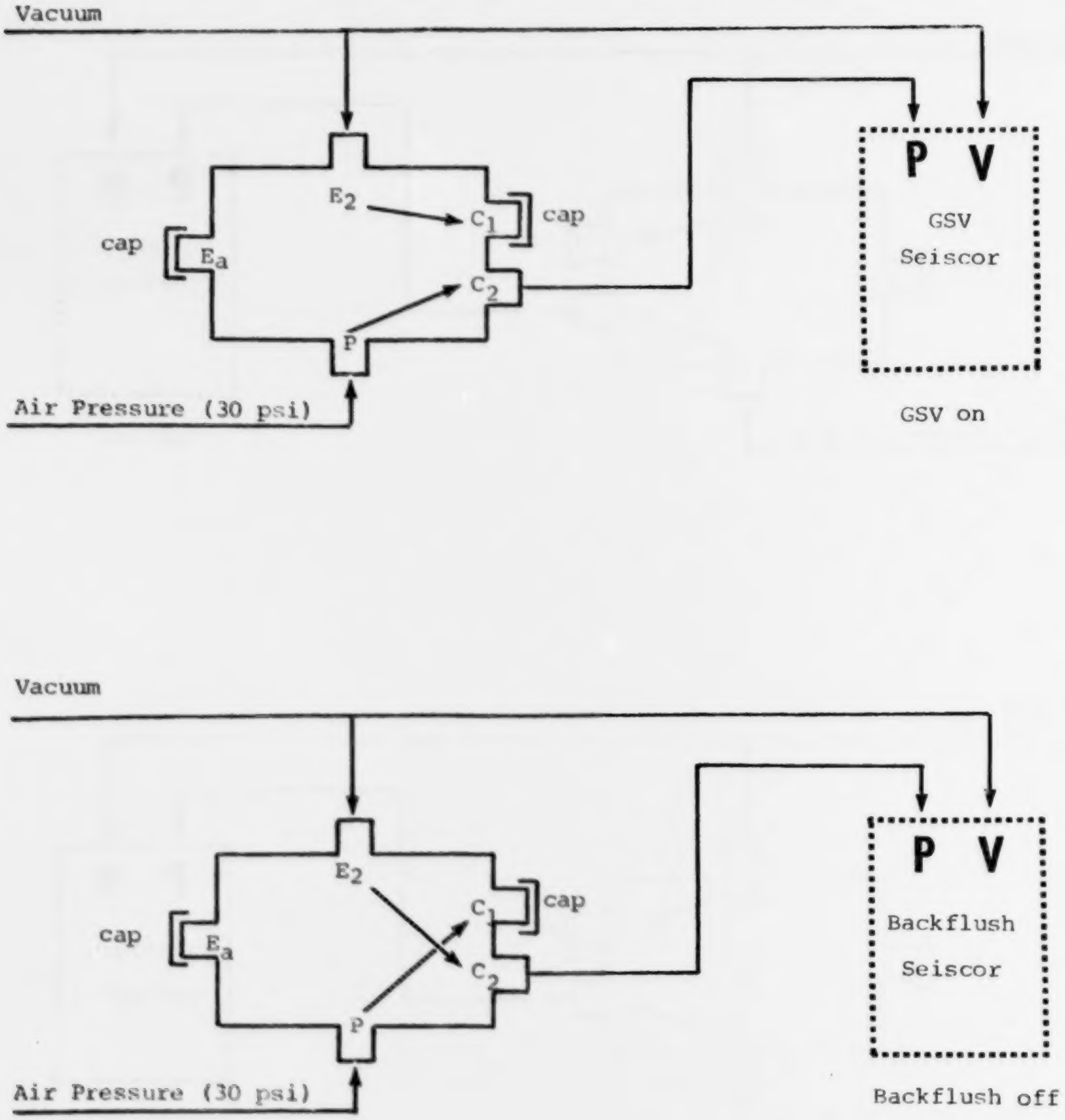
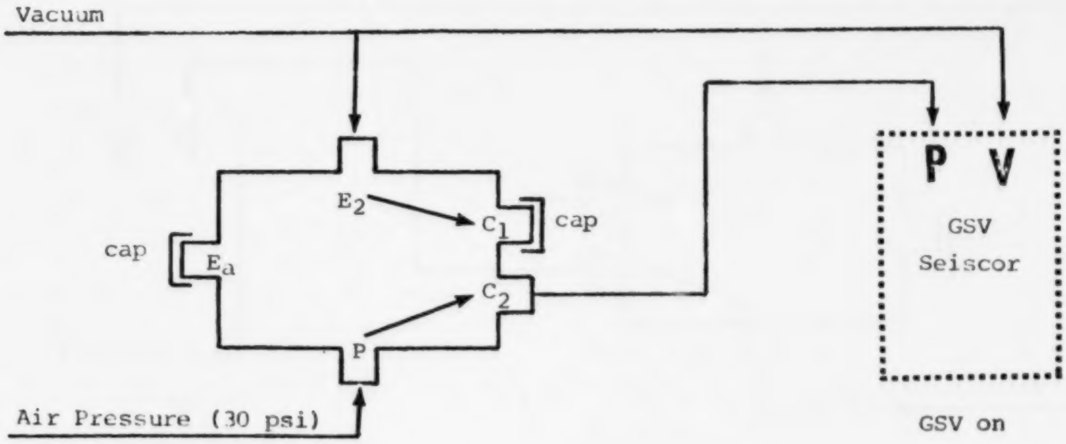

Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
GSV
Seiscor
GSV on
Vacuum
E2
C1
cap
cap
Ea
C2
P
Air Pressure (30 psi)
P V
Backflush
Seiscor
Backflush off

Figure 10. Flow schematic in electric solenoid valves (GSV energized, backflush de-energized).


Vacuum
E_2
C_1
cap
cap
E_a
C_2
P
Air Pressure (30 psi)
P
V
GSV
Seiscor
GSV on

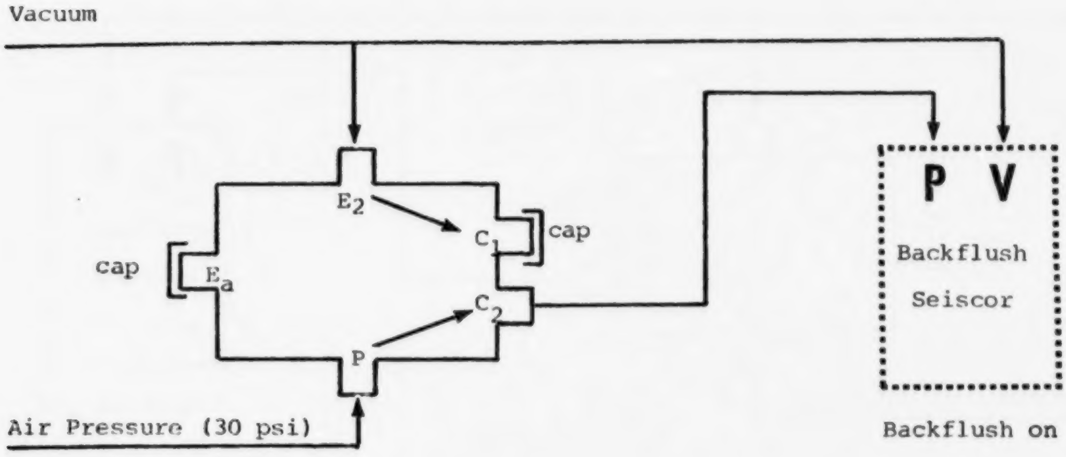

Vacuum
E_2
C_1
cap
cap
E_a
C_2
P
Air Pressure (30 psi)
P
V
Backflush
Seiscor
Backflush on

Figure 11. Flow schematic in electric solenoid valves
(Both valves energized).

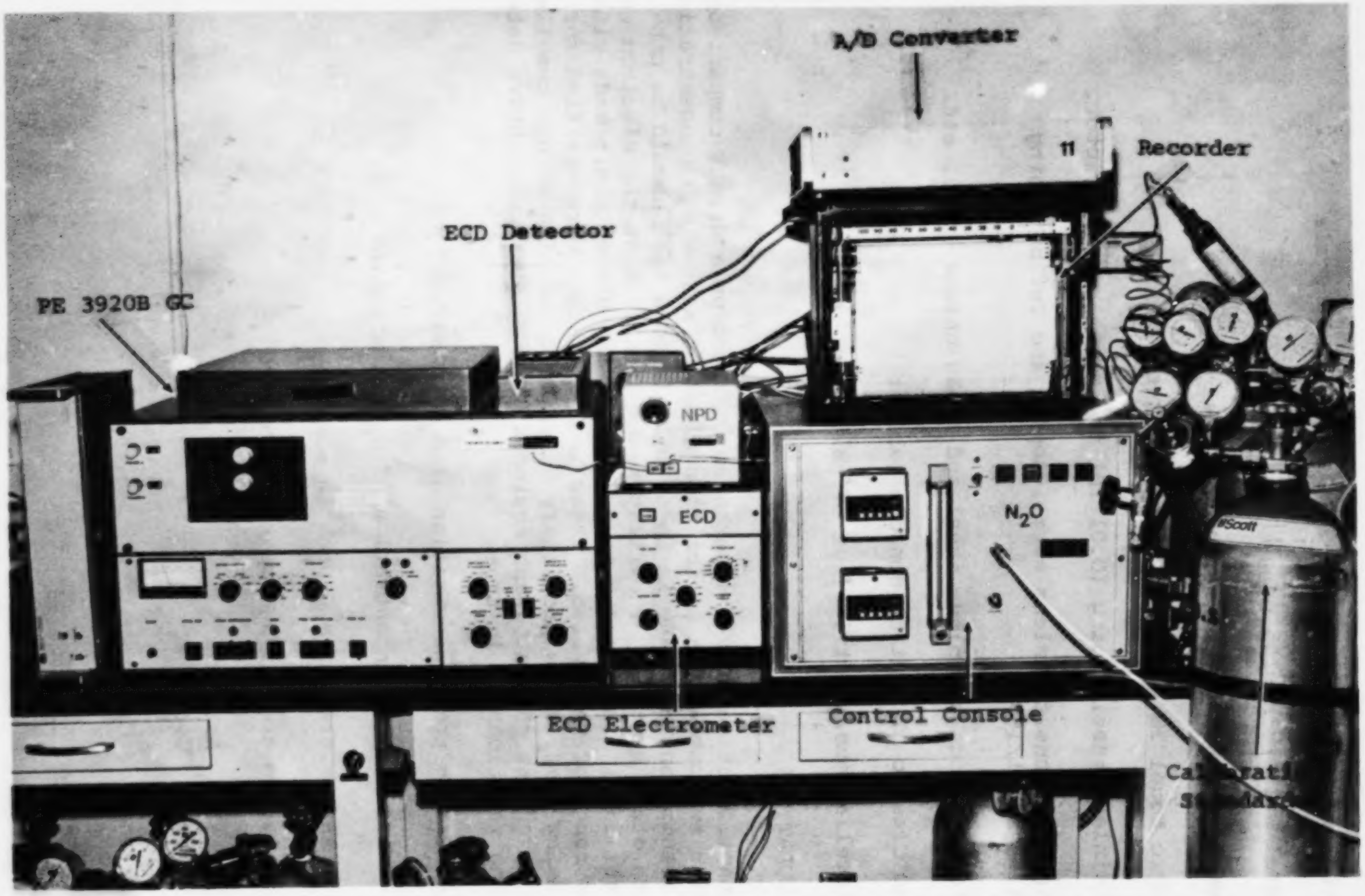

A/D Converter
11
Recorder
ECD Detector
PE 3920B GC
NPD
ECD
N_2O
Scott
ECD Electrometer
Control Console
Calibration Standard

Figure 12. Nitrous oxide analytical system.

5. Stripper column, 2' x 1/8" SS, 10% OV-17 on 80/100 Gas Chrom Q

6. ASCO solenoid valve, Model 834501 (2 ea)

7. Brook flowmeter, R-2-15-A w/SS float, 0-150 scale

8. Metal Bellows MB-155 pump

9. Female quick-connect, stainless steel

10. Nupro Model 2M stainless steel regulating valve

11. Stainless steel tubing (0.01"ID) for capillary restrictor.

12. Miscellaneous stainless steel, copper and Teflon tubing (1/8" and 1/16")

13. Miscellaneous stainless steel and brass unions, tees, etc.

14. Bud Classic II control console cabinet

15. Miscellaneous electrical on-off switches.

SAMPLE CALCULATIONS

The quantification of N_2O in exhaust is based on a direct comparison of the N_2O in exhaust with a calibration blend of a know N_2O concentration. Two basic assumptions are made in these calculations that should be considered with other systems. The first assumption is that the electron capture detector has a linearized output and that measurements are made within the working range of the system. These two parameters were verified for this procedure using instruments previously described. Working within the linear range of a given gas chromatograph equipped with an electron capture detector, the following relationship is true.

Let Csam = ppm concentration of N_2O in sample

Cstd = ppm concentration of N_2O in standard

Asam = area of N_2O peak in sample

Astd = area of N_2O peak in standard

$$\frac{\text{Astd}}{\text{Cstd}} = \frac{\text{Asam}}{\text{Csam}}$$

Solving for Csam

$$\text{Csam} = \frac{\text{Asam} \times \text{Cstd}}{\text{Astd}}$$

Example 1:

A 4.95 ppm N_2O (in nitrogen) calibration blend was found to give 5291 area counts for the N_2O peak. An exhaust sample was found to give 2674 area counts for the N_2O peak. Calculate the N_2O in the exhaust sample.

$$Csam = \frac{Asam \times Cstd}{Astd}$$

$$Csam = \frac{2674 \times 4.95}{5291}$$

$$Csam = 2.50 \text{ ppm } N_2O$$

Example 2:

A 1.13 ppm N_2O (in nitrogen) calibration blend was found to give 1208 area counts for the N_2O peak. An exhaust sample was found to give 534 area counts for the N_2O peak. Calculate the concentration of N_2O in the exhaust sample.

$$Csam = \frac{Asam \times Cstd}{Astd}$$

$$Csam = \frac{534 \times 1.13}{1208}$$

$$Csam = 0.50 \text{ ppm } N_2O$$

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Porapak Brochure, Waters Associates, Framingham, Mass.

Bethea, R., and Adams, F., J. Chromatog., Vol. 10, pg. 1, 1963.

Leithe, W., *The Analysis of Air Pollutants*, Humphrey Sci. Pub., Ann Arbor, Michigan, 1970, pg. 176.

Private communication between Dr. R. B. Zweidinger and Frank Black.

LaHue, M. D., Axelrod, H. D., and Lodge Jr., J. P., Anal. Chem, Vol. 43, pg. 1113, 1974.

APPENDIX F

INDIVIDUAL HYDROCARBON PROCEDURE

THE MEASUREMENT OF INDIVIDUAL HYDROCARBONS IN EXHAUST

This procedure was developed to measure individual hydrocarbons in dilute automotive exhaust. The term, individual hydrocarbons (IHC) is used to define the collection of compounds: methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2), propane (C_3H_8), propylene (C_3H_6), benzene (C_6H_6), and toluene (C_7H_8). Dilute exhaust is collected in Tedlar bags during a test cycle and analyzed with a gas chromatographic system containing four separate columns and a flame ionization detector (FID). The peak areas are compared to an external calibration blend and individual hydrocarbon concentration are analyzed with a Hewlett-Packard 3354 computer system. The analysis flow schematic is shown in Figure 1.

ANALYTICAL SYSTEM

The analysis for individual hydrocarbons is conducted with a Varian Aerograph Series 1400 gas chromatograph using a flame ionization detector (FID). Four separate packed columns are used to resolve these individual compounds. An elaborate system of timers, solenoid valves, and gas sampling valves are used to direct the flow of the sample through the system. The actual analytical system is shown in Figure 2.

The first two columns are used to resolve air, methane, ethylene, ethane, acetylene, propane and propylene, respectively; while columns III and IV resolve benzene and toluene. Column I consists of an 8' x 1/8" stainless steel tube packed with Porapak Q 80/100 mesh. This column is primarily used to resolve methane from air. It undergoes temperature programming from 25°C to 100°C at 12°/min. Column II consists of a 4' x 1/8" Teflon column packed with 35/60 mesh type 58 Silica gel. C_2 and C_3 hydrocarbons are resolved with this column. It is held isothermal at room temperature (20°C). The third column is used to resolve benzene from the other aromatics, paraffins, olefins, and acetylenes. It consists of a 15' x 1/8" stainless steel column packed with 15 percent 1, 2, 3-tris (2-cyanoethoxy) propane on 60/80 mesh Chromosorb PAW. This column is held isothermal at 100°C at the end of the temperature program sequence. Column IV is a 2' x 1/8" stainless steel tube packed with 40 percent mercury sulfate ($HgSO_4$) and 20 percent sulfuric acid (H_2SO_4) on Chromosorb W. This column resolves benzene and toluene from the oxygenated hydrocarbons such as aldehydes and ketones. It is also held isothermal at room temperature for the entire analysis sequence. All samples pass through a 6' x 0.01" capillary restrictor before entering the detector. Helium is the carrier gas with a column flow of 52 mℓ/min.

The temperature program sequence is accomplished with the oven of the gas chromatograph. Columns I and III are in this oven although Column I is the only one used during the temperature program. The gas sampling valves

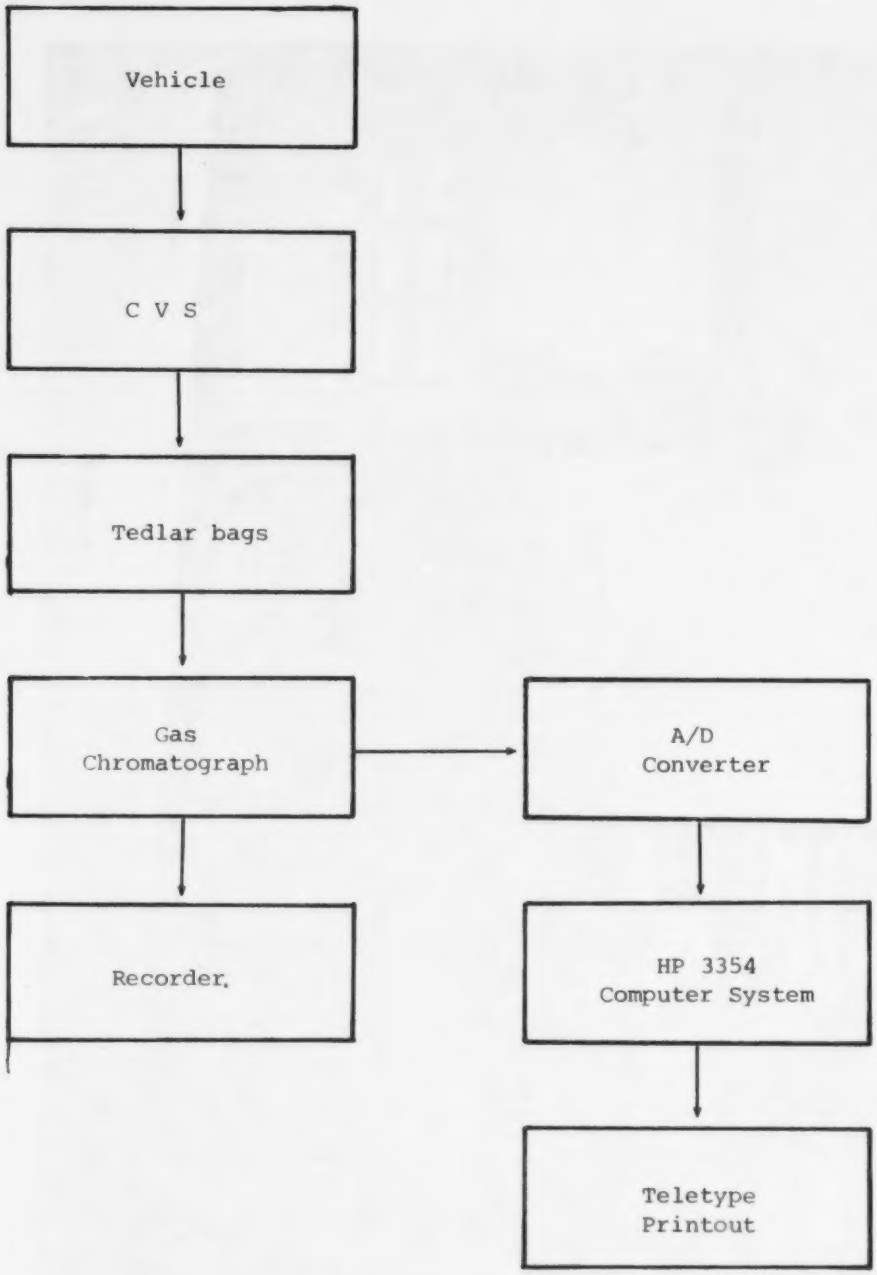

Vehicle
C V S
Tedlar bags
Gas Chromatograph
A/D Converter
Recorder.
HP 3354 Computer System
Teletype Printout

Figure 1. The analysis flow schematic for individual hydrocarbons.

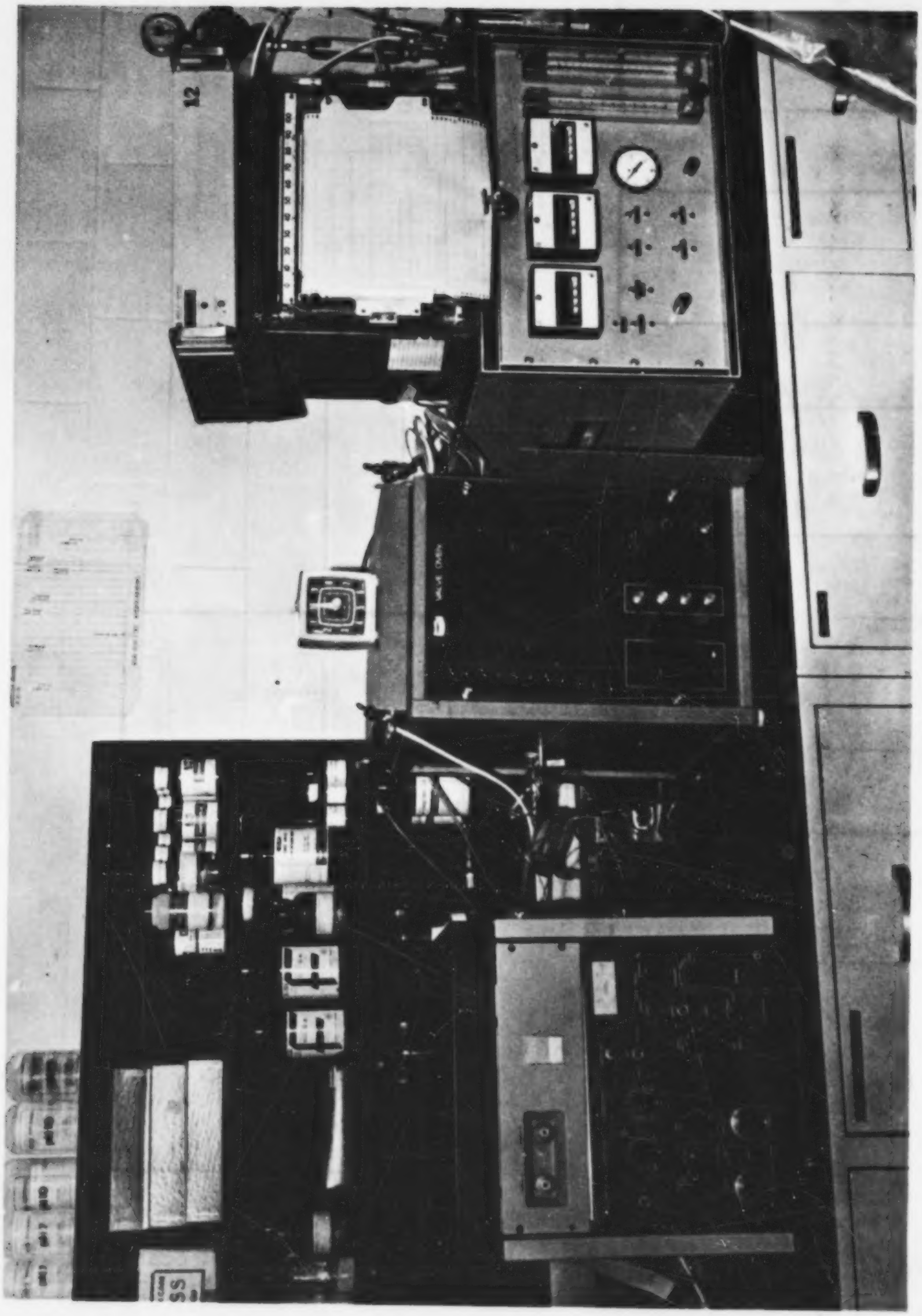


Figure 2. Analytical system for individual hydrocarbons.

are contained in a Bendix Valve Oven. The temperature is maintained at 100°C. Columns II and IV are external to this oven for isothermal room temperature operation.

Samples are collected in Tedlar bags during the driving cycle along with a background bag. The sample is purged through two 10 mℓ sample loops for four (4) minutes. At this time, the initial configuration of the analytical system is shown in Figure 3. Upon injection, gas sampling valve A is activated by solenoid valve G, the temperature program sequence is started, and the first timer begins to count down 680 seconds. The temperature program sequence for Columns I and II starts at 25°C and increases at 12°/min to a final temperature of 100°C. Columns I and III are held isothermal at this temperature for the remainder of the analysis. The configuration of the analytical system is shown in Figure 4. The sample in the first loop passes through Columns I and II and into the detector. The peaks (in the order of elution) are air, methane, ethylene, ethane, acetylene, propane and propylene. After 680 seconds, the second step begins with solenoid H activating gas sampling valve B. The second timer begins to count down 120 seconds. At this time, the sample trapped in the second 10 mℓ sample loop is channeled through Column III. The analytical system configuration is shown in Figure 5. After 120 seconds, step 3 begins. The third timer starts counting down 480 seconds and gas sampling valves C and J are activated by solenoid valve E. Columns I and II are backflushed through a capillary restrictor to the vent and Columns III and IV are directed to the detector. The configuration is shown in Figure 6. After 480 seconds, solenoid valve F activates gas sampling valve D. Column III is backflushed through a capillary restrictor to the vent. The final configuration is shown in Figure 7. The last two peaks in the order of elution are benzene and toluene. Upon elution of the last peak, the system is reset to the initial position.

A time/temperature system operation sequence is presented in Figure 8. The solid line on this graph represents the gas chromatograph oven temperature during the temperature program sequence. The time at which each step begins is also represented on the graph.

Figures 9 through 13 illustrate a simplified version of the flow of the carrier gas and sample through the gas sampling valves. Figure 9 shows the configuration of the gas sampling valves in the sample purge position. The sample is pumped out of the sample bag and through the sample loops. Column III is flushing and Column IV is backflushing to the vent and Columns I and II are directed to the detector. At the start of an injection, the position of gas sampling valve A changes and the trapped sample is directed to Columns I and II. Columns III and IV remain in the flushing mode. Figure 10 illustrates the analytical configuration upon injection. Step 2 begins with the trapped sample in sample loop B routed to Column III. Figure 11 demonstrates Step 2. Gas sampling valves C and J are simultaneously switched to backflush Columns I and II and direct the sample in sample loop B through Column III and Column IV and then to the detector in Step 3. Finally, Step 4 results in the backflushing of Column III to the vent. The system remains in this configuration until it is reset to the initial purge position. A sample chromatogram for the calibration blend of individual hydrocarbons is shown in Figure 14.

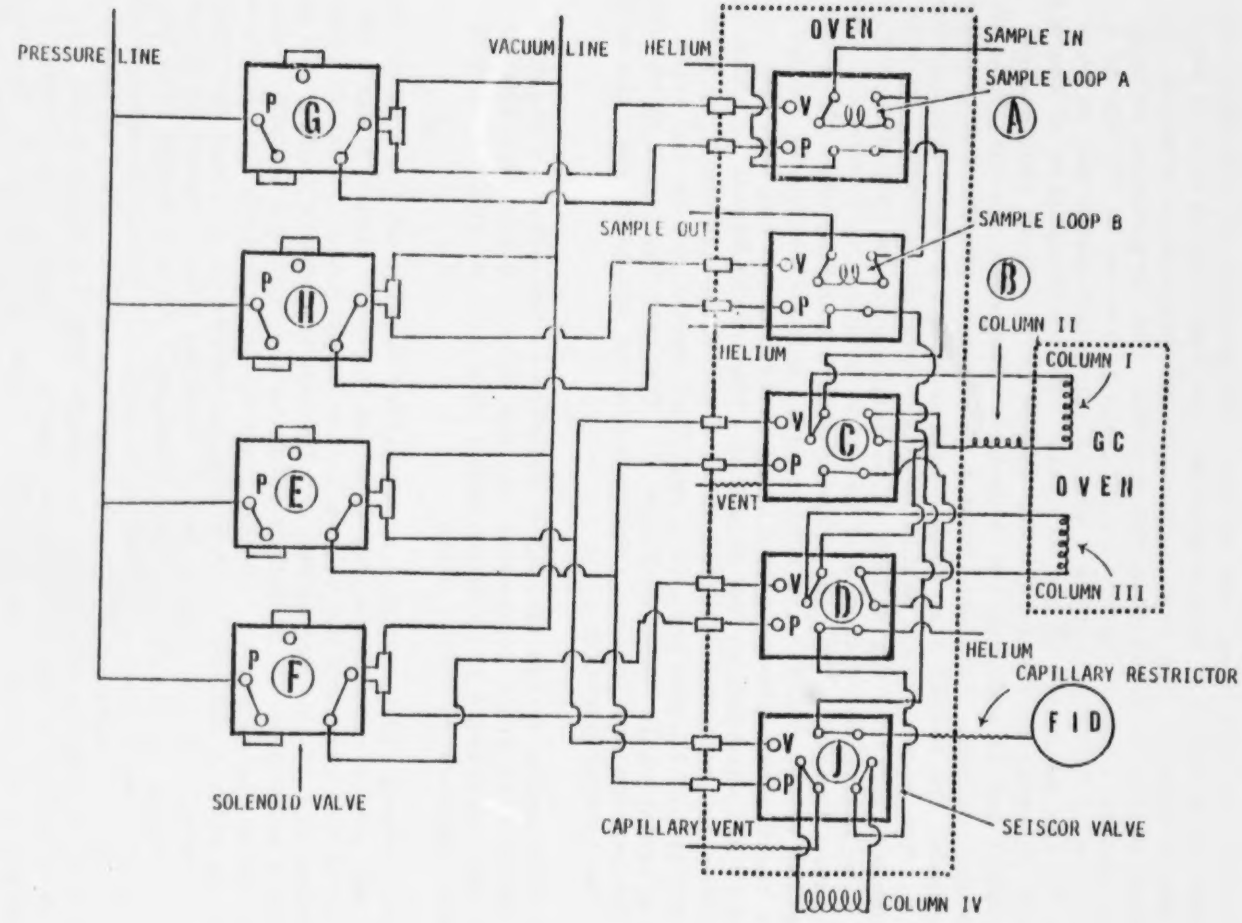

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
G
V
P
SAMPLE OUT
SAMPLE LOOP B
B
H
HELIUM
COLUMN II
COLUMN I
GC
OVEN
C
E
VENT
COLUMN III
D
HELIUM
CAPILLARY RESTRICTOR
F
J
FID
SOLENOID VALVE
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV

Figure 3. Initial analytical system configuration.

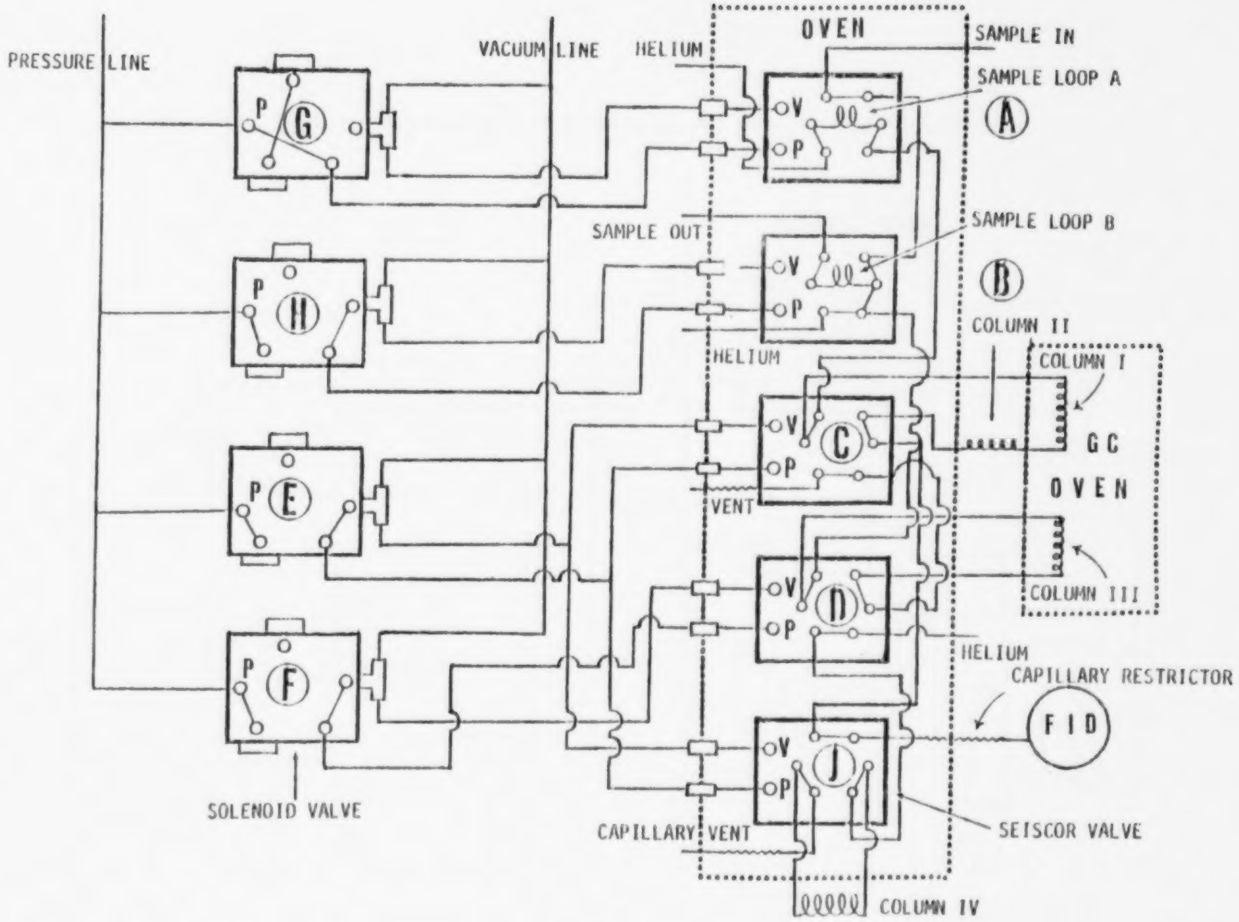

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
SAMPLE OUT
SAMPLE LOOP B
B
HELIUM
COLUMN II
COLUMN I
GC
OVEN
COLUMN III
VENT
HELIUM
CAPILLARY RESTRICTOR
FID
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV
SOLENOID VALVE
G
H
E
F
C
D
J
P
V

Figure 4. Step 1 solenoid G activation of gas sampling valve A.

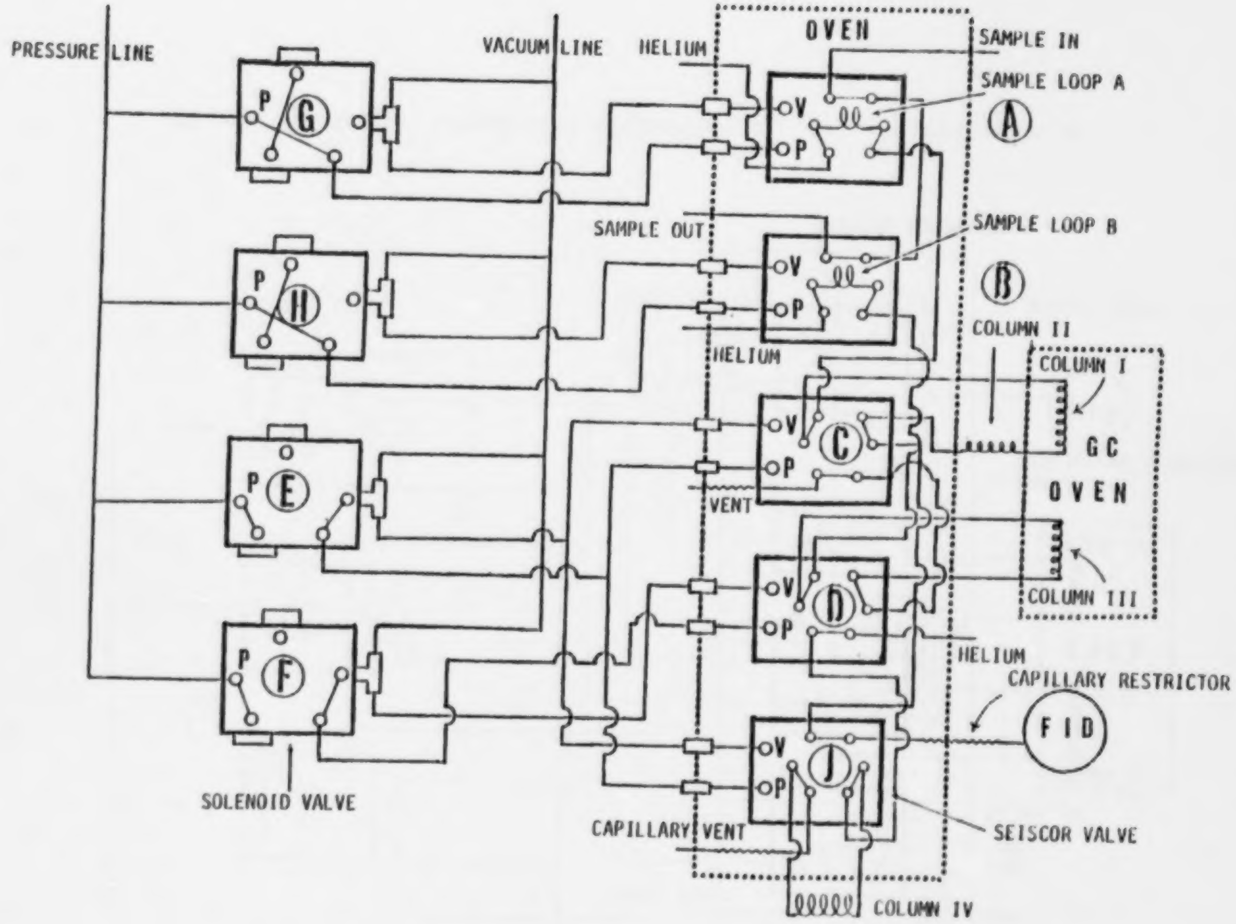

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
SAMPLE OUT
SAMPLE LOOP B
B
HELIUM
COLUMN II
COLUMN I
GC
OVEN
COLUMN III
VENT
HELIUM
CAPILLARY RESTRICTOR
FID
SOLENOID VALVE
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV
G
H
E
F
C
D
J
P
V

Figure 5. Step 2 solenoid H activation of gas sampling valve B.

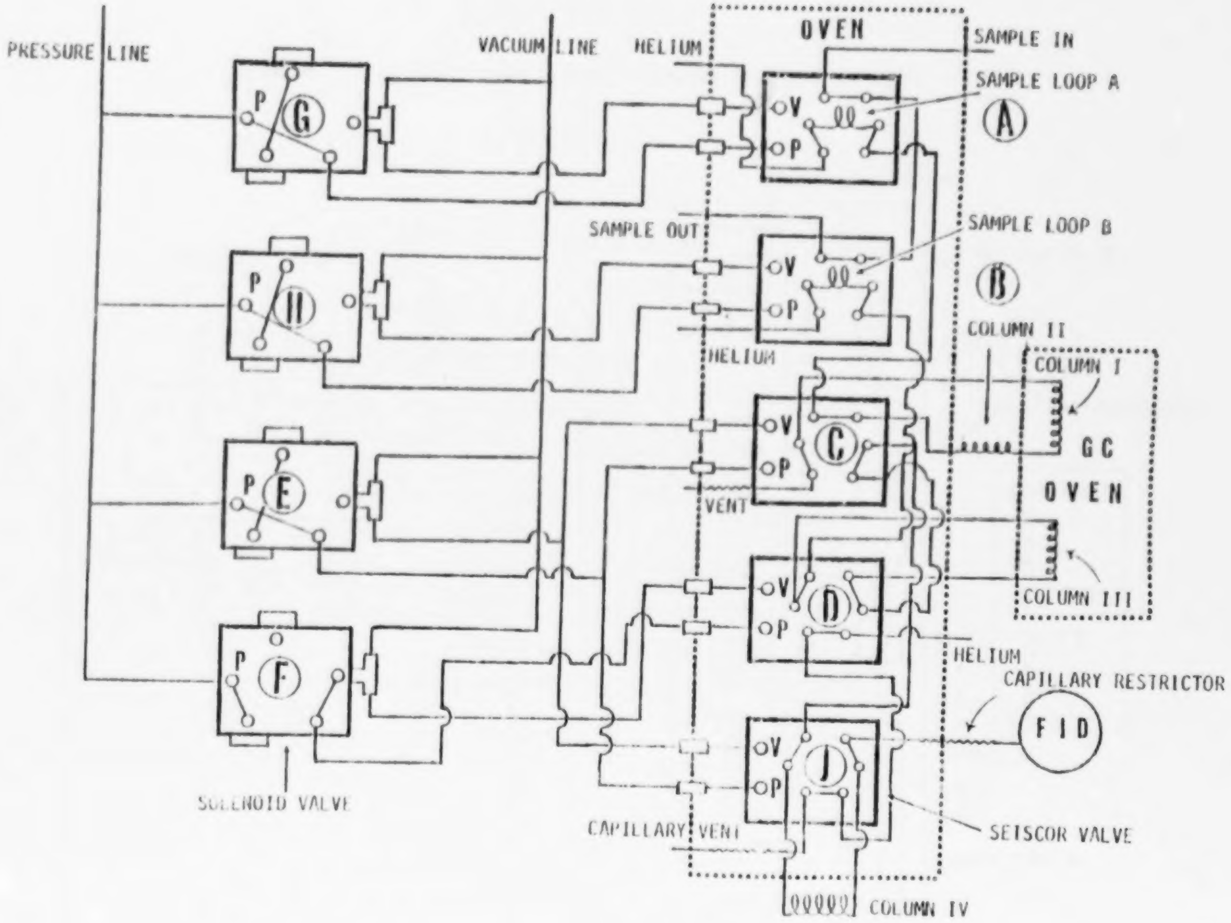

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
G
SAMPLE OUT
SAMPLE LOOP B
B
H
HELIUM
COLUMN II
COLUMN I
GC
OVEN
C
E
VENT
COLUMN III
D
F
HELIUM
CAPILLARY RESTRICTOR
FID
J
SOLENOID VALVE
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV
V
P

Figure 6. Step 3 solenoid E activation of gas sampling valves C and J.

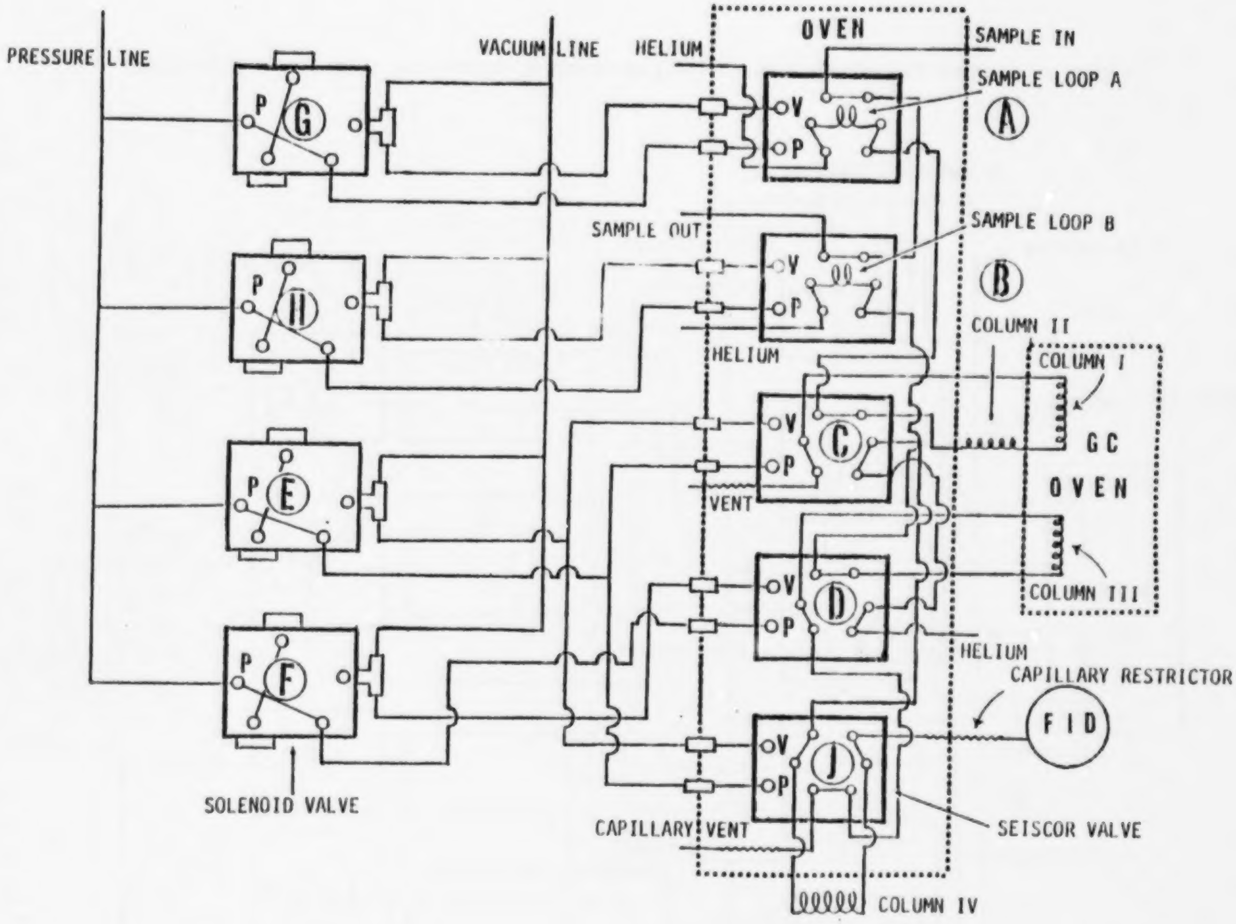

PRESSURE LINE
VACUUM LINE
HELIUM
OVEN
SAMPLE IN
SAMPLE LOOP A
A
G
P
V
P
SAMPLE OUT
SAMPLE LOOP B
B
H
HELIUM
COLUMN II
COLUMN I
GC
OVEN
C
E
VENT
COLUMN III
D
HELIUM
CAPILLARY RESTRICTOR
F
FID
J
SOLENOID VALVE
CAPILLARY VENT
SEISCOR VALVE
COLUMN IV

Figure 7. Final analytical system configuration.

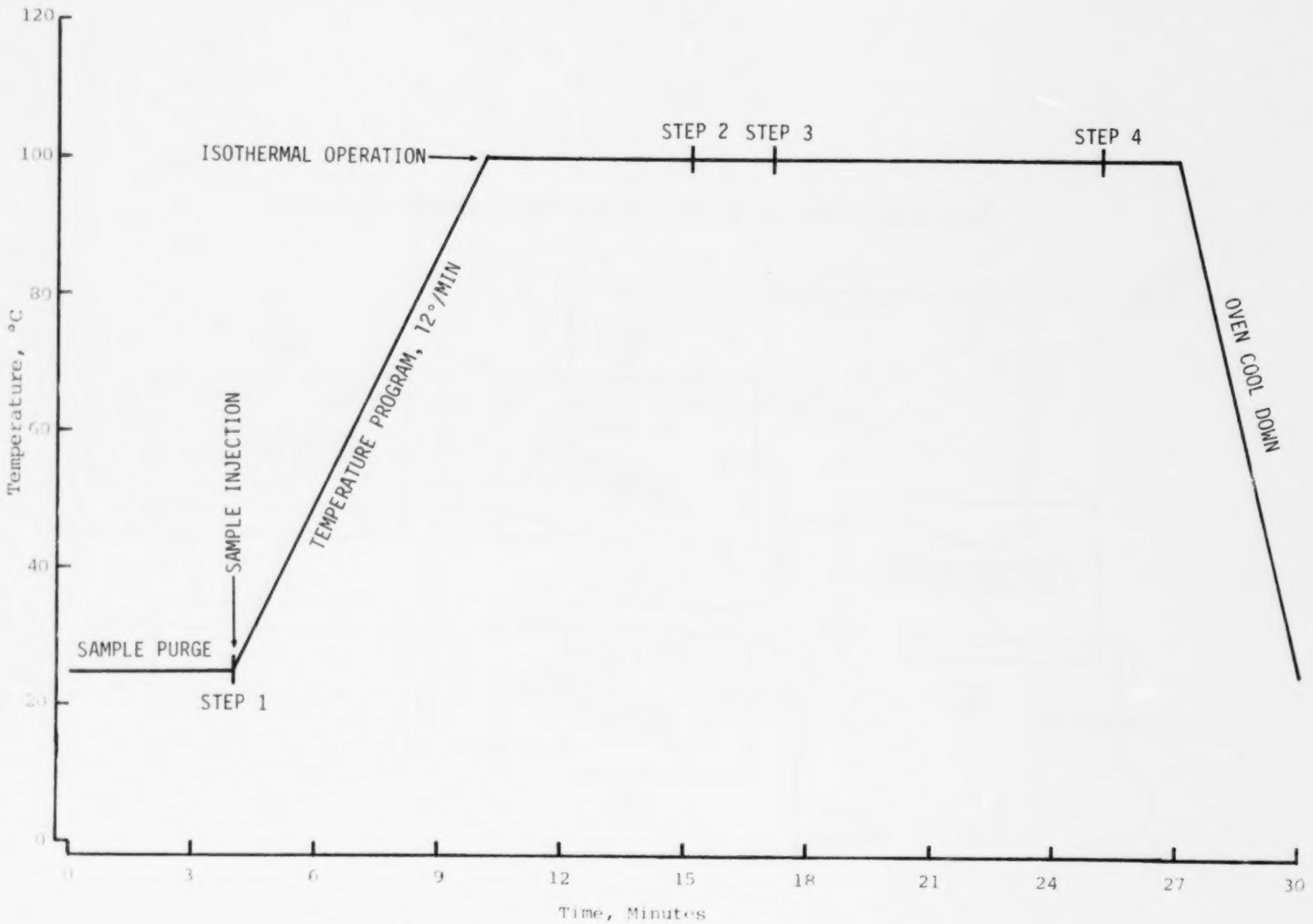


Figure 8. System operation sequence.

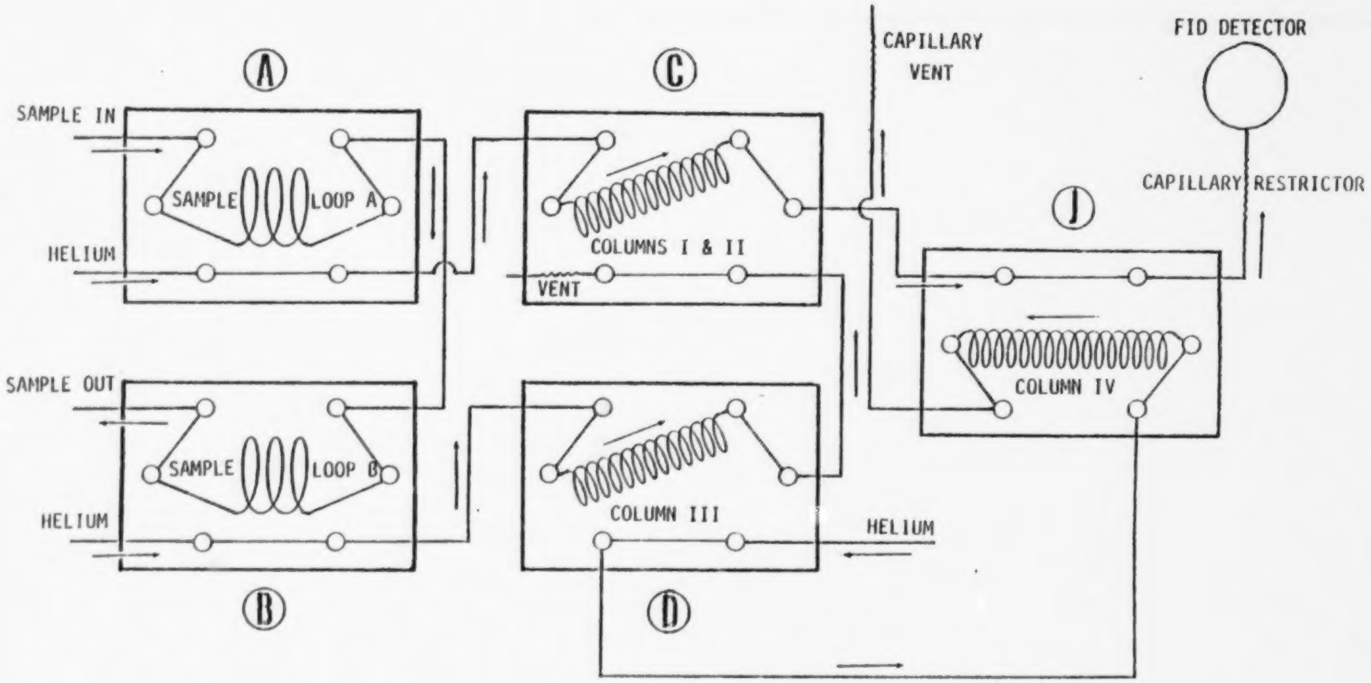

Ⓐ
SAMPLE IN
SAMPLE
LOOP A
HELIUM
Ⓒ
COLUMNS I & II
VENT
CAPILLARY
VENT
FID DETECTOR
CAPILLARY RESTRICTOR
Ⓙ
COLUMN IV
SAMPLE OUT
SAMPLE
LOOP B
HELIUM
Ⓑ
COLUMN III
HELIUM
Ⓓ

Figure 9. Sample purge position prior to sample injection.

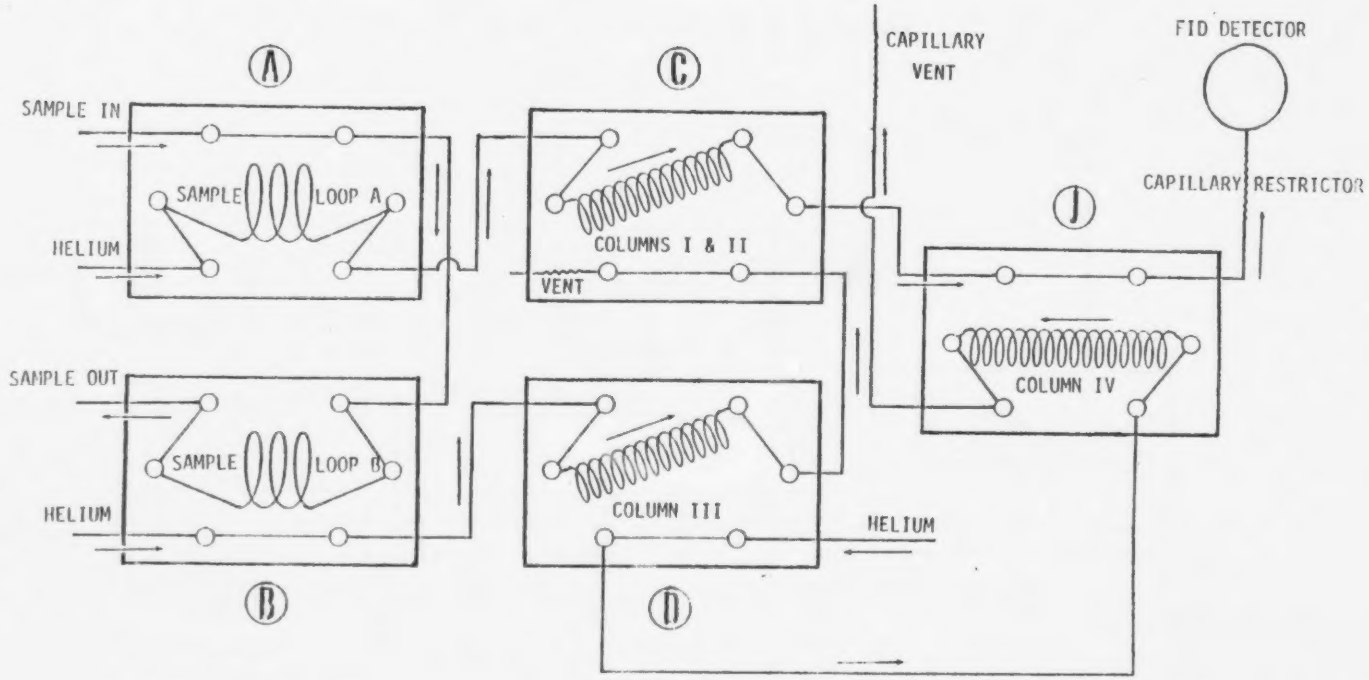

Ⓐ
SAMPLE IN
SAMPLE
LOOP A
HELIUM
Ⓒ
COLUMNS I & II
VENT
CAPILLARY
VENT
FID DETECTOR
CAPILLARY RESTRICTOR
Ⓙ
COLUMN IV
SAMPLE OUT
SAMPLE
LOOP B
HELIUM
Ⓑ
COLUMN III
HELIUM
Ⓓ

Figure 10. Step 1 sample loop A injected.

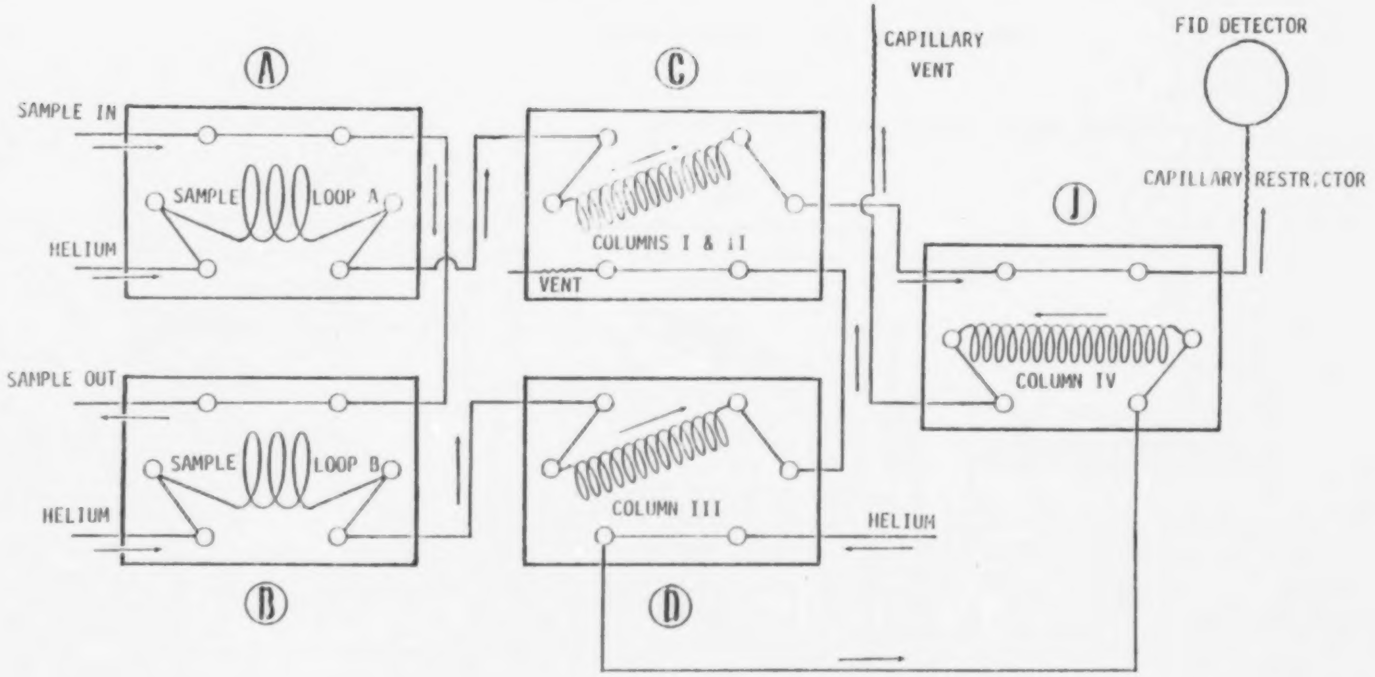
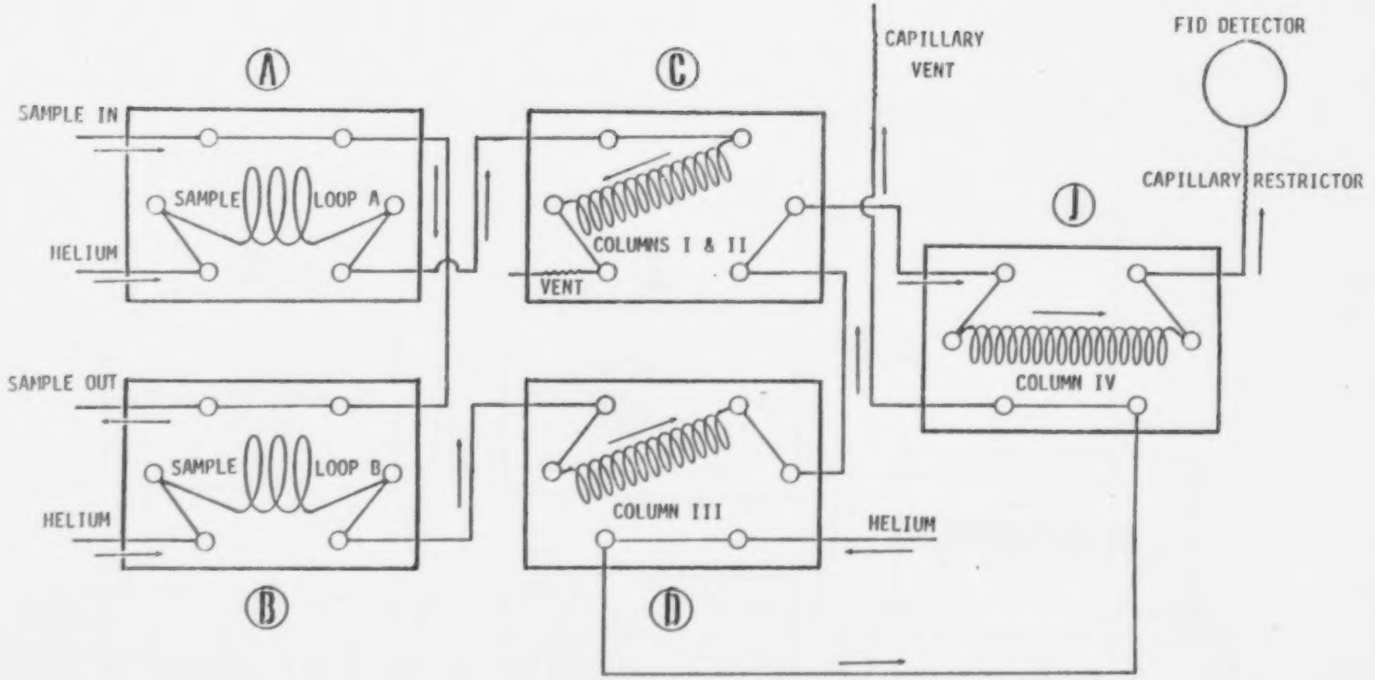

A
C
CAPILLARY
VENT
FID DETECTOR
SAMPLE IN
SAMPLE
LOOP A
HELIUM
COLUMNS I & II
VENT
CAPILLARY RESTRICTOR
J
COLUMN IV
SAMPLE OUT
SAMPLE
LOOP B
HELIUM
COLUMN III
HELIUM
B
D

Figure 11. Step 2 sample loop B injected.



Ⓐ
SAMPLE IN
SAMPLE
LOOP A
HELIUM
Ⓒ
COLUMNS I & II
VENT
CAPILLARY VENT
FID DETECTOR
CAPILLARY RESTRICTOR
Ⓙ
COLUMN IV
SAMPLE OUT
SAMPLE
LOOP B
HELIUM
Ⓑ
COLUMN III
HELIUM
Ⓓ

Figure 12. Step 3 simultaneous solenoid C and J activation.

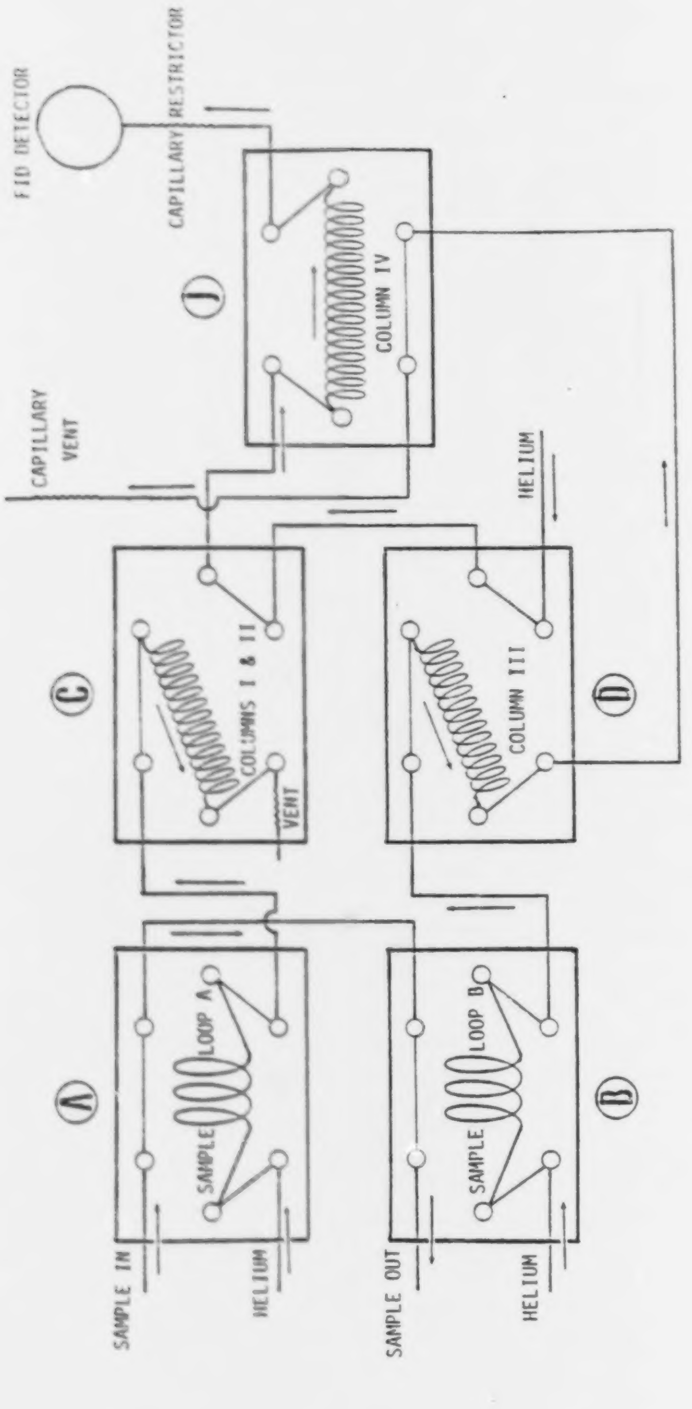

FID DETECTOR
CAPILLARY RESTRICTOR
CAPILLARY VENT
COLUMN IV
C
COLUMNS I & II
VENT
HELIUM
D
COLUMN III
A
SAMPLE LOOP A
SAMPLE IN
HELIUM
B
SAMPLE LOOP B
SAMPLE OUT
HELIUM

Figure 13. Step 4 backflushing of column III.

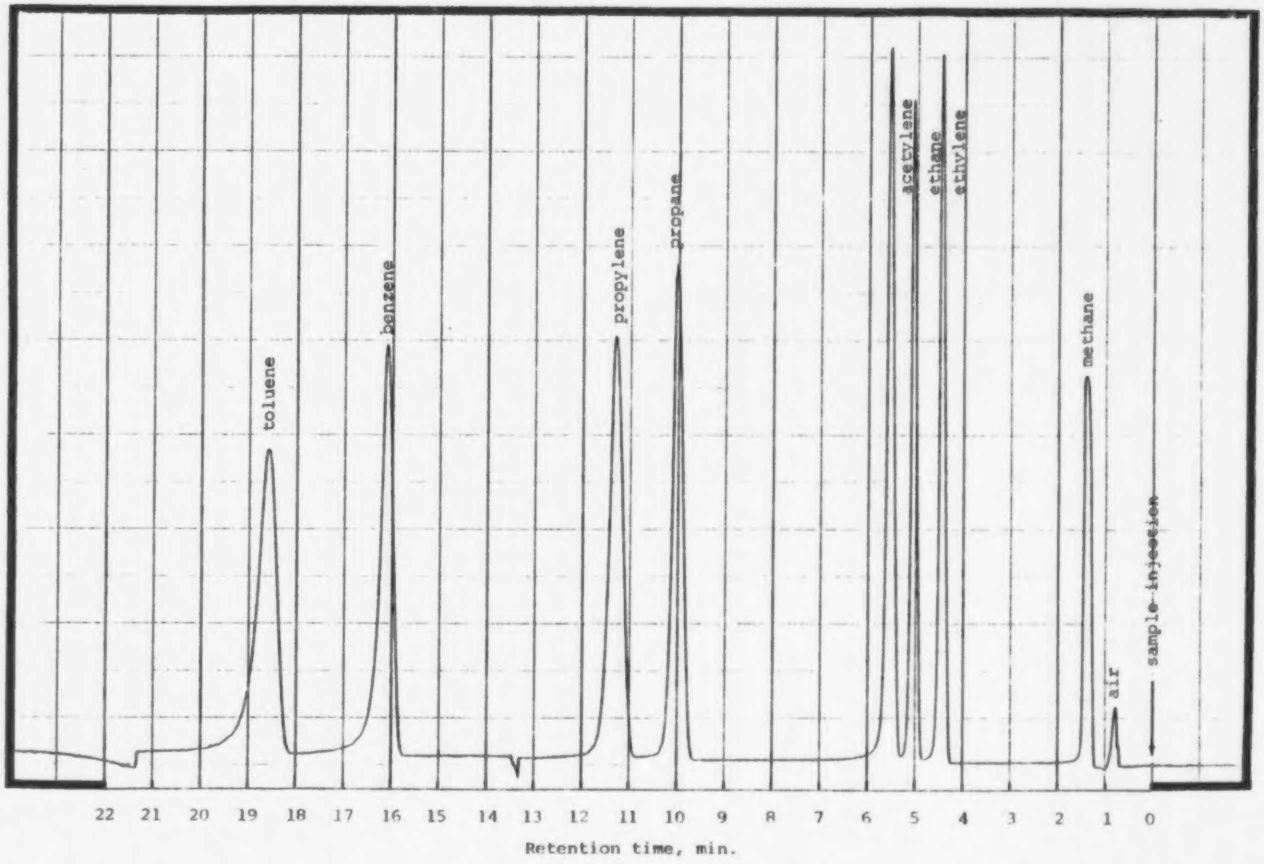


Figure 14. Calibration blend for specific hydrocarbons.

CONTROL SYSTEM

The control of the five Seiscor gas sampling valves is accomplished by ATC timers and ASCO electric solenoid valves. With the solenoid valve in the de-energized configuration, the gas sampling valve is in one position. An electrical impulse from the timer energizes the solenoid valve. The pressure difference created in the gas sampling valve changes the position. Figure 15 illustrates the de-energized and energized configuration for solenoid valve G and gas sampling valve A. This accomplishes the complicated column flow sequence required for this analysis. The system analytical repeatability is ± 1.8 percent.

EQUIPMENT

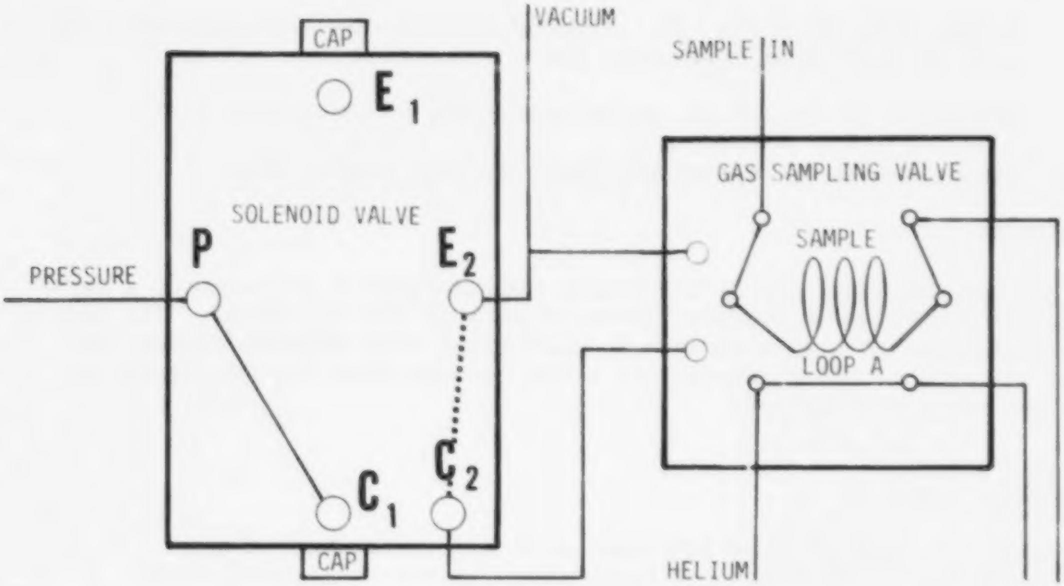
This analysis is performed using a gas chromatograph equipped with a flame ionization detector (FID). The equipment required is divided into two categories. The major items in each category are listed below:

Gas Chromatograph Detection

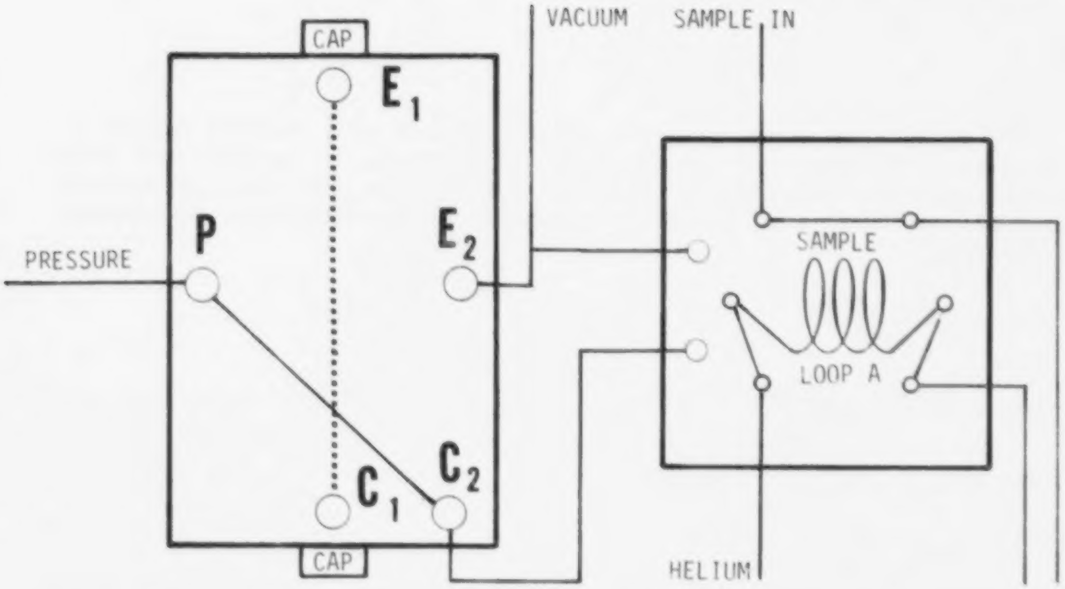
1. Varian Aerograph Series 1400 Gas Chromatograph
2. Leeds and Northrup 1 mv Recorder
3. Hewlett-Packard Model 3354 Computer System
4. Hewlett-Packard Model 1865A A/D Converter

Control Console System

1. Seiscor Model VIII Gas Sampling Valve
2. ATC Timers, Model 325A346A10PX
3. ASCO 4-way Midget Solenoid Valve, No. 8345B
4. Thomas Sample Pump, Model 106 CA18
5. Brooks Flowmeter, R-2-15-AAA with glass float, 0-15 Scale
6. Miscellaneous stainless steel and brass nuts, ferrules, unions, tees, connectors, etc.
7. Miscellaneous stainless steel, copper, and Teflon tubing
8. Bendix Valve Oven
9. Column I, 8' x 1/8" SS, 80/100 mesh Porapak Q
10. Column II, 4' x 1/8" Teflon, 35/60 mesh Type 58 Silica Gel


VACUUM
SAMPLE IN
CAP
E1
GAS SAMPLING VALVE
SOLENOID VALVE
SAMPLE
P
E2
PRESSURE
LOOP A
C2
C1
CAP
HELIUM

de-energized configuration


VACUUM
SAMPLE IN
CAP
E1
P
E2
SAMPLE
PRESSURE
LOOP A
C2
C1
CAP
HELIUM

energized configuration

Figure 15. Solenoid valve G with gas sampling valve A.

11. Column III, 15' x 1/8" SS, 15 percent 1,2,3-tris (cyanoethoxy) Propane on 60/80 Mesh Chromosorb PAW

12. Column IV, 2' x 1/8" SS, 40 percent $HgSO_4$ on Chromosorb W

13. Miscellaneous electrical switches, wiring, lights, etc.

CALCULATIONS

The concentration of the individual hydrocarbons is compared to a calibration blend with known concentrations of each of the components. The peak areas are determined with a Hewlett-Packard Model 3354 computer system and printed out on a remote teletype unit. The concentration of the sample is determined with the equation:

$$\frac{Astd}{Cstd} = \frac{Asam}{Csam}$$

where Astd = the peak area of component n in the calibration blend
Cstd = the concentration of component n in the calibration blend
Asam = the peak area of component n in the sample
Csam = the unknown concentration of component n in the sample
n = the component of interest (i.e., methane, ethylene, ethane, acetylene, propane, propylene, benzene, or toluene)

If the equation is solved of Csam, the result is:

$$Csam = \frac{Asam \times Cstd}{Astd}$$

Example 1:

A bag sample was taken from the exhaust stream of a vehicle during a driving cycle. The peak area of the calibration blend for methane was 11893 area counts with a concentration of 13.616 ppm C. The peak area of methane in the sample was 8593 area counts. Calculate the concentration of methane in the exhaust.

$$Csam = \frac{Asam \times Cstd}{Astd}$$

$$Csam = \frac{(8593)\ (13.616)}{(11893)}$$

Csam = 9.84 ppm C for methane

Example 2:

In the sample analysis, the peak area for toluene was 10973 area counts. The peak area for the calibration blend was 18546 area counts for toluene with a concentration of 21.272 ppm C. Calculate the concentration of toluene in the sample.

$$\text{Csam} = \frac{\text{Asam x Cstd}}{\text{Astd}}$$

$$\text{Csam} = \frac{(10973)\ (21.272)}{(18546)}$$

Csam = 12.59 ppm C for toluene

Note: These sample calculations are presented as an example only and are not necessarily representative of expected values in exhaust.

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APPENDIX G

HYDROGEN SULFIDE PROCEDURE

THE MEASUREMENT OF HYDROGEN SULFIDE IN EXHAUST

The measurement of hydrogen sulfide in dilute automotive exhaust is accomplished by collecting the dilute exhaust in glass impingers. The absorbing solution is a buffered zinc acetate solution which traps the sulfide ion as zinc sulfide. The exhaust is collected continuously during the entire test cycle. Upon completion of the test, the absorbing solution is treated with N,N dimethyl-paraphenylene diamine sulfate and ferric ammonium sulfate. Cyclization occurs forming the highly colored heterocyclic compound methylene blue (3,9-bisdimethylaminophenazothionium sulfate). The resulting solution is analyzed with a spectrophotometer at 667 nm in a 1 cm or 4 cm pathlength cell depending upon the concentration. The minimum detectable concentration is 0.01 ppm.

SAMPLING SYSTEM

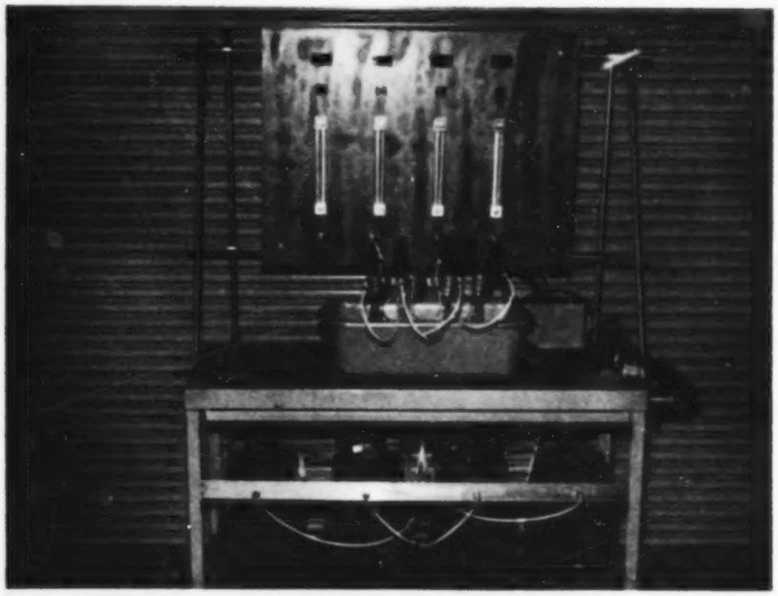
Dilute automotive exhaust samples are collected with the sampling system shown in Figure 1. With this sampling system, the sample is removed from the stream of dilute exhaust. A flow schematic of the sampling system is shown in Figure 2. A solenoid valve is used to open and close the sampling system from the CVS. The sample is bubbled through the absorbing solution to remove H_2S. A series of two glass impingers is sufficient to collect 99+ percent of H_2S from the sample. The temperature of the absorbing solution is maintained at 0-5°C with an ice bath slurry. The gas stream is passed through a drier to remove any moisture. A pump capable of pulling a flow rate of at least 4 ℓ/min pulls the sample through the system. The dry gas meter measures the volume of dried gas that has passed through the system during each test cycle. The proper flow rate of 4 ℓ/min is continuously monitored with a flowmeter. The gas stream is then vented to the atmosphere. This sampling system provides an efficient means of trapping the dilute sample and enables rapid chemical analysis of the trapped sample.

LIST OF EQUIPMENT

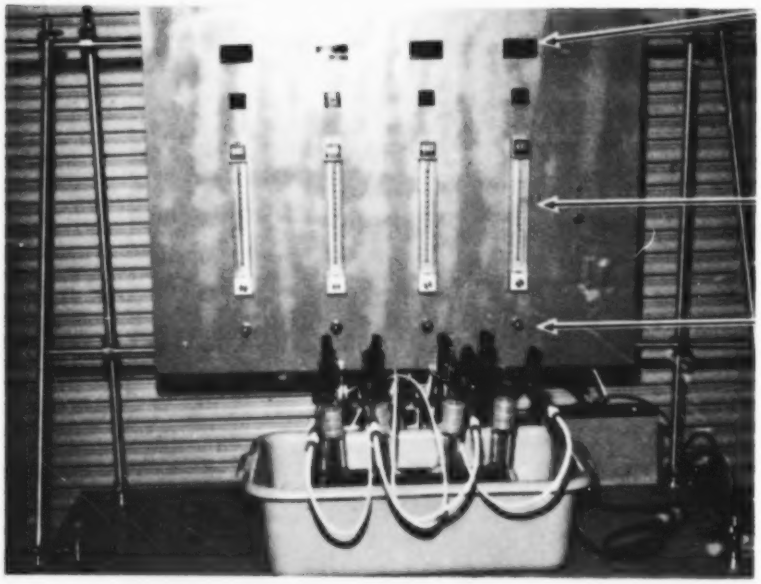
The equipment required in this analysis is divided into two basic categories. The first category involves the sample acquisition using the glass impingers. The second category contains equipment related to the analysis of the sample once it has been obtained. The individual items in each category are listed below:

Sample Acquisition

1. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 ℓ/min.

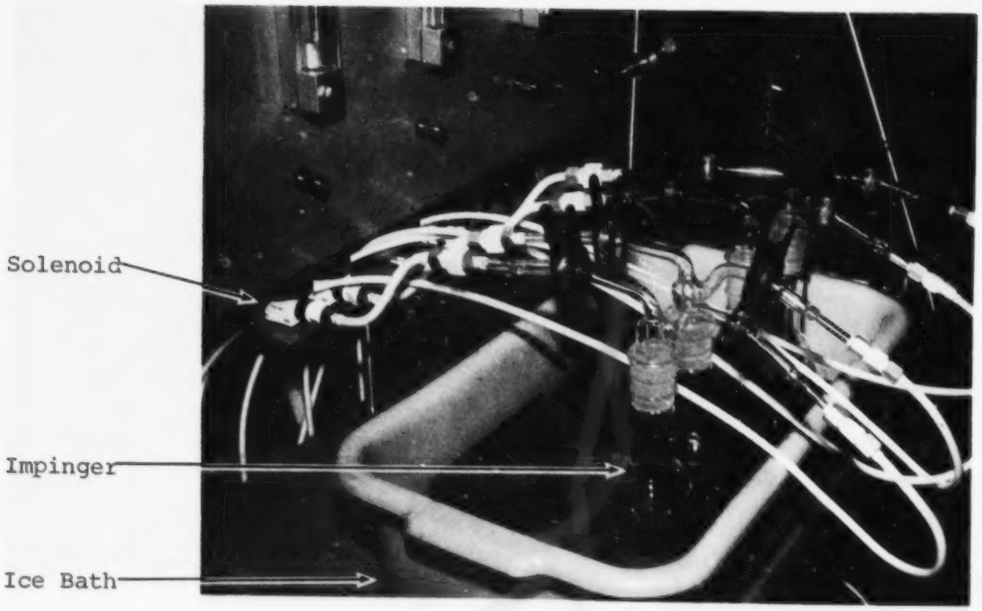


Front View

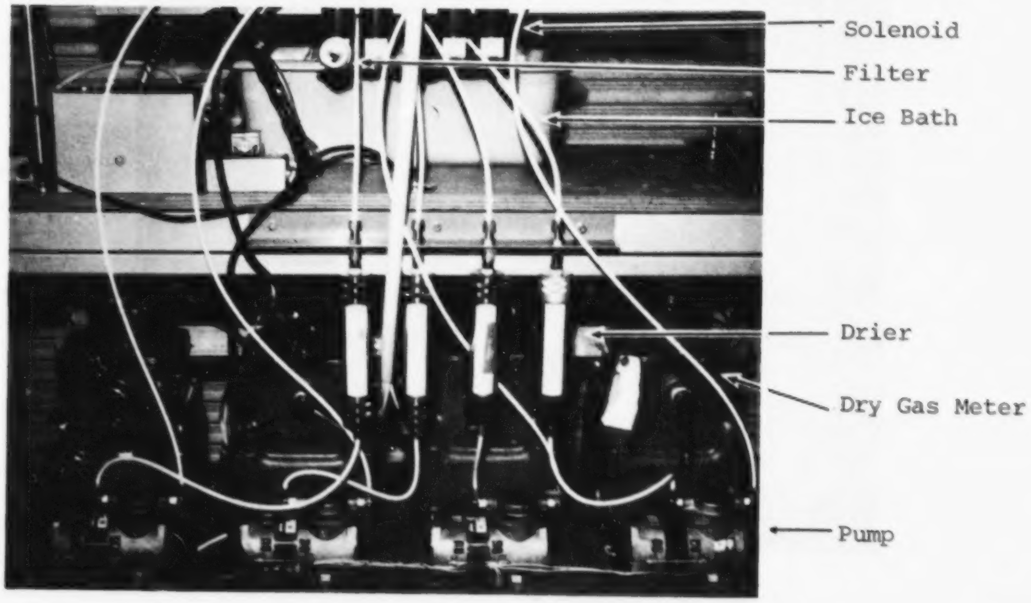

Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 1. The dilute exhaust sampling system for hydrogen sulfide.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 1 (Cont'd). The dilute exhaust sampling system for hydrogen sulfide.

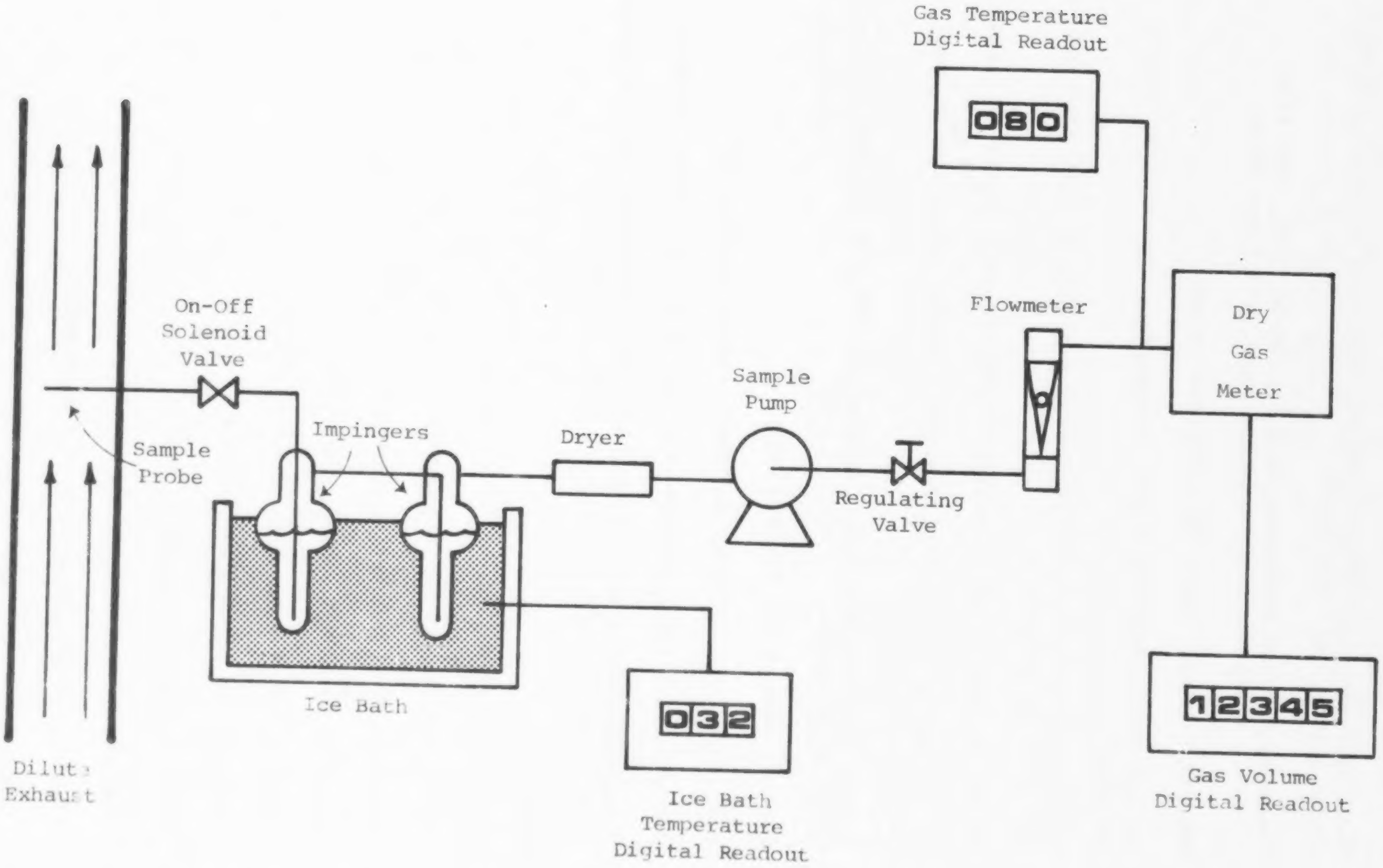

Gas Temperature
Digital Readout
080
On-Off
Solenoid
Valve
Flowmeter
Dry
Gas
Meter
Sample
Pump
Impingers
Dryer
Sample
Probe
Regulating
Valve
Ice Bath
032
12345
Dilute
Exhaust
Ice Bath
Temperature
Digital Readout
Gas Volume
Digital Readout

Figure 2. Hydrogen sulfide sample collection flow schematic.

2. Glass impingers, Ace Glass Products, Catalog No. 7530-11, 29/42 bottle joints, 18/7 arm joints.
3. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/min range.
4. Regulating valve, Nupro 4MG, stainless steel.
5. Dry gas meter, American Singer Corporation, Type Al-120, 60 CFH capacity.
6. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" OD x 3/16" ID.
7. Teflon solenoid valve, The Fluorocarbon Company, Model DV2-144NCA1.
8. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.
9. Drying tube, Analabs, Inc., Catalog No. HGC-146, 6" long, 1/4" brass fittings.
10. Digital readout for dry gas meter.
11. Miscellaneous electrical switches, lights, wiring, etc.
12. Six-channel digital thermometer, Analog Devices, Model 2036/J/1.
13. Iron/constantan Type J, Thermo Sensors Corporation, single thermocouple, 1/4" OD stainless steel metal sheath.

Sample Preparation

1. Pipet-aid, Order No. JX-7290.
2. Class A, 10 mℓ volumetric pipets.
3. Class A, 15 mℓ volumetric pipets.
4. Class A, 20 mℓ volumetric pipets.
5. Class A, 25 mℓ volumetric pipets.
6. Class A, 100 mℓ volumetric flask.
7. Class A, 500 mℓ volumetric flask.
8. Class A, 1000 mℓ volumetric flask.
9. Class A, 25 mℓ burets with Teflon stopcock.
10. Class A, 100 mℓ graduated cylinder.

11. Micro burets, 5 mℓ with Teflon stopcock.

12. Erlenmeyer flask, 250 mℓ.

13. Erlenmeyer flask, 500 mℓ.

14. Dropping bottle, 60 mℓ with ground glass pipet and rubber bulb.

15. Beaker, 100 mℓ.

16. Repipet dispenser, 2 mℓ.

17. Repipet dispenser, 10 mℓ.

18. Centrifuge tube, 15 mℓ.

19. Watch glass.

Instrumental Analysis

1. Beckman Model 25 spectrophotometer with recorder.

2. One cm pathlength disposable curvettes, CI regular.

3. Beckman UV silica cell, 40 mm pathlength, No. 580016.

LIST OF REAGENTS

This procedure requires the sample collection in glass impingers with a buffered zinc acetate absorbing solution (0.25 M zinc acetate and 0.10 M sodium acetate). An amine reagent (0.005 M N,N dimethyl-para-phenylene diamine sulfate and 3.50 M sulfuric acid) and a ferric ion solution (0.25 M ferric ammonium sulfate and 0.5 M sulfuric acid) are mixed with the absorbing solution. Sodium sulfide is used as the standard. An iodometric titration is used to standardize the sodium sulfide. All of the reagents used in preparing these solutions are listed below along with the manufacturer and the quality.

1. Zinc acetate, dihydrate formula weight = 219.49; chemical formula = $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, crystal, "Baker Analyzed" reagent.

2. Sodium acetate, anhydrous formula weight = 82.03; chemical formula = $NaC_2H_3O_2$, analytical reagent grade, powder, Mallinckrodt Code 7372.

3. N,N-dimethyl-pphenylene diamine sulfate, formula weight = 370.47; chemical formula = $(NH_2C_6H_4N(CH_3)_2)_2 \cdot H_2SO_4$, 98 percent minimum by titration and spectro analysis, Eastman Code 1333.

4. Sulfuric acid, formula weight = 98.08; chemical formula = H_2SO_4, ACS analytical reagent grade, Mallinckrodt Code 2876.

5. Ferric ammonium sulfate, formula weight = 482.19; chemical formula = $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$, ACS analytical reagent grade, crystals, Mallinckrodt Code 5064.

6. Sodium sulfide, formula weight = 240.18; chemical formula = $Na_2S \cdot 9H_2O$, ACS analytical reagent grade, crystals, Mallinckrodt Code 8044.

7. Iodine, formula weight = 253.81; chemical formula = I_2, ACS analytical reagent grade, resublimed, Mallinckrodt Code 1008.

8. Hydrochloric acid, formula weight = 36.46; chemical formula = HCl, ACS reagent, assay 36.5-38.0 percent HCl, Eastman Code 13061.

9. Sodium thiosulfate, formula weight = 248.18; chemical formula = $Na_2S_2O_3 \cdot 5H_2O$, ACS analytical reagent grade, crystals, Mallinckrodt Code 8100.

10. Starch soluble; chemical formula = $(C_6H_{10}O_5)n$, certified ACS, powder, Fisher Code S-516.

11. Arsenic trioxide primary standard, formula weight = 197.82; chemical formula = As_2O_3, powder, ACS analytical reagent, Mallinckrodt Code 3668.

12. Potassium iodide, formula weight = 166.01; chemical formula = KI, compacted crystal, "Baker Analyzed" reagent.

13. Sodium hydroxide pellets, formula weight = 40.00; chemical formula = $NaOH$, caustic soda, ACS analytical reagent grade, Mallinckrodt Code 7708.

14. Sodium bicarbonate, formula weight = 84.01; chemical formula = $NaHCO_3$, powder, ACS analytical reagent grade, Mallinckrodt Code 7412.

15. Sodium carbonate anhydrous powder, formula weight = 105.99; chemical formula = Na_2CO_3, ACS analytical reagent grade, Mallinckrodt Code 7521.

16. Potassium dichromate, crystal, primary standard, formula weight = 294.22; chemical formula = $K_2Cr_2O_7$, "Baker Analyzed" reagent.

17. Litmus test paper, blue, reagent ACS, Fisher Code 14-875.

18. Glycerol, formula weight = 92.10; chemical formula = $HOCH_2CH(OH)CH_2OH$, ACS analytical reagent, Mallinckrodt Code 5092.

PREPARATION OF REAGENTS

The various reagents needed for the analysis of hydrogen sulfide can be divided into two separate categories. The first category includes the reagents for sample acquisition and color development. The other category encompasses the standard solutions and solutions used for standardization. The chemicals used to make these solutions are ACS analytical reagent grade with the exception of potassium dichromate and arsenic trioxide which are a primary reagent grade.

Sample Acquisition and Color Development

Absorbing Reagent -- The absorbing reagent is prepared by dissolving 54.9 g (0.25 mole) of zinc acetate, 8.2 g (0.10 mole) of sodium acetate, and 40 mℓ (0.56 mole) glycerol, in vacuum boiled, deionized water and diluted to 1 liter. A 2 mℓ portion of 0.05 M sodium sulfide solution is added dropwise to the diluted solution with vigorous shaking. This removes traces of heavy metals by precipitating them as their insoluble sulfides. This solution is then set aside overnight. The resulting solution is filtered through a fine textured paper with the first 50 mℓ portion being discarded. This solution is stable for at least one (1) week. A gradually developing cloudiness is of no consequence.

Amine Solution -- A 0.005 M solution is prepared by dissolving 0.93 g of N,N dimethyl-para-phenylene diamine sulfate in 75 mℓ of deionized water. Then, 197 mℓ of concentrated sulfuric acid is slowly added and the mixture is allowed to cool. The resulting solution is diluted to 1 liter with deionized water. This solution is stable for about six (6) months.

Ferric Ion Solution -- The ferric ion solution is prepared by dissolving 120.6 g (0.25 mole) of ferric ammonium sulfate in 750 mℓ of deionized water. A 27 mℓ portion of concentrated sulfuric acid is added and the solution is allowed to cool before diluting to 1 liter with deionized water. The solution is stable for one (1) month.

Standards and Standardization Solutions

Sulfide Standard Solution -- Approximately 8 g (0.03 mole) of sodium sulfide is rinsed with vacuum boiled, deionized water to remove traces of sulfide from the surface of the crystals. The crystals are then dissolved in vacuum boiled, deionized water and diluted to 1 liter to give a concentrated solution. A more dilute solution of sulfide ion is prepared by diluting 10 mℓ of the concentrated solution to 1 liter with vacuum boiled, deionized water. This solution is standardized by iodometric titration. The approximate concentration is 10 ppm sulfide ion by weight. This solution should be prepared immediately before use.

Thiosulfate Standard Solution -- Approximately 2.5 g (0.01 mole) of sodium thiosulfate is dissolved in 500 mℓ of freshly vacuum boiled, deionized water in a 1 liter volumetric flask. A 0.1 g (0.001 mole) portion of sodium carbonate is added and the solution is stirred until dissolved. The solution is then diluted to 1 liter and stored in the dark. Addition of a small amount of sodium carbonate prevents the formation of hydrogen sulfite ion from thiosulfate ion in the presence of acid. The addition of such substances as chloroform, sodium benzoate, or mercury (II) iodide inhibits the growth of bacteria. This solution is stable for several weeks but should be discarded if it becomes turbid. It is standardized with a potassium dichromate primary standard.

Starch Indicator -- The indicator is prepared by making a paste of 0.5 g of soluble starch in 2 or 3 mℓ of deionized water. The resulting slurry is slowly poured into 50 mℓ of boiling deionized water and heated until clear (about 2-3 minutes). The solution is then cooled and centrifuged for several minutes. The supernatant liquid is decanted into a clean, 60 mℓ reagent bottle equipped with a pipet. This aqueous starch solution will decompose due to bacterial action in several days. This can be prevented by storing the indicator under sterile conditions, the addition of mercury (II) iodide to inhibit the bacterial action, or by preparing fresh daily.

Iodine Solution -- About 25 g (0.15 mole) of potassium iodide is dissolved in 10 mℓ of deionized water. Then, 12.7 g (0.05 mole) of iodine crystals are added and dissolved with occasional stirring. The solution is filtered and diluted to 1 liter with deionized water. The resulting solution is approximately 0.1 N and is used to prepare the 0.01 N solution. The 0.1 N solution is standardized against arsenic trioxide. The dilute iodine solution is prepared by diluting 10 mℓ of the 0.1 N solution to 100 mℓ with deionized water. This solution is standardized with a previously standardized thiosulfate solution. The dilute iodine solution is prepared and standardized daily because of the volatility of iodine and oxidation by dissolved oxygen.

DESCRIPTION OF METHOD

Hydrogen sulfide is collected in a buffered zinc acetate absorbing reagent from dilute automotive exhaust. The highly colored species, methylene blue, is generated by the addition of N,N dimethyl-para-phenylene diamine sulfate and ferric ion. Methylene blue has an absorbance maxima in the red region of the visible spectrum. The extinction wavelength curve for methylene blue is shown in Figure 3.

The analytical procedure for the determination of hydrogen sulfide in dilute automotive exhaust consists of two major areas. The first is the standardization and calibration of the standard sulfide ion solution. The second area includes the sample acquisition and color development of the hydrogen sulfide sample. Each will be discussed in detail below. The analysis flow schematic for this procedure is shown in Figure 4.

Standardization and Calibration

The thiosulfate solution is standardized against primary standard grade potassium dichromate. The potassium dichromate is dried in an oven at 150° to 200°C for 1 to 2 hours. A weighed 0.10 to 0.15 g (0.001 mole) portion of dried potassium dichromate is placed in a 500 mℓ Erlenmeyer flask and dissolved in 50 mℓ of deionized water. A freshly prepared solution of 3 g (0.02 mole) of potassium iodide, 5 mℓ of 6 N hydrochloric acid and 50 mℓ of deionized water is then added. This solution is gently swirled, covered with a watch glass, and allowed to stand for five (5) minutes. The sides of the flask are then washed with deionized water followed by approximately 200 mℓ of deionized water. The resulting solution is titrated with the standardized

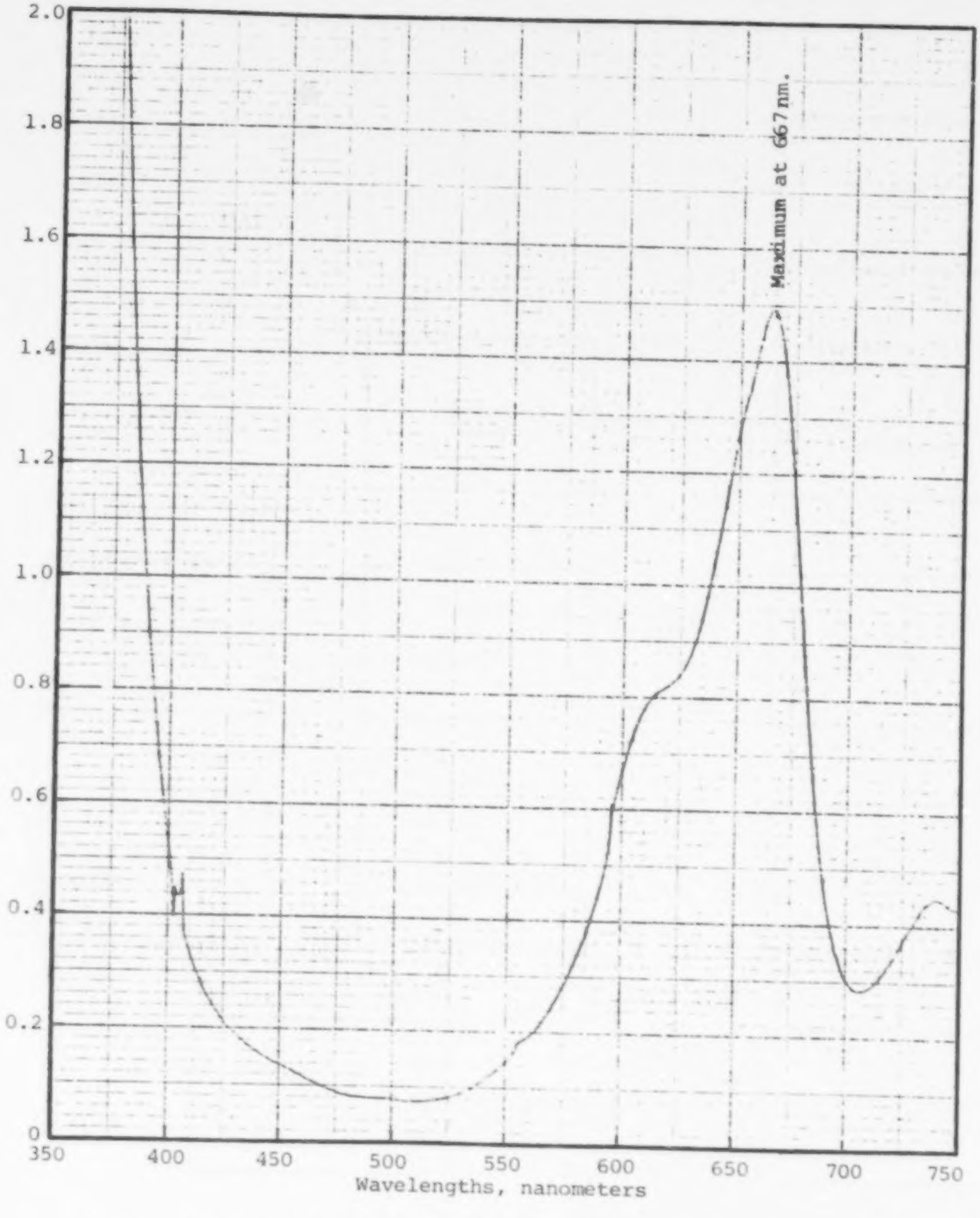


Figure 3. Extinction-wavelength curve of methylene blue.

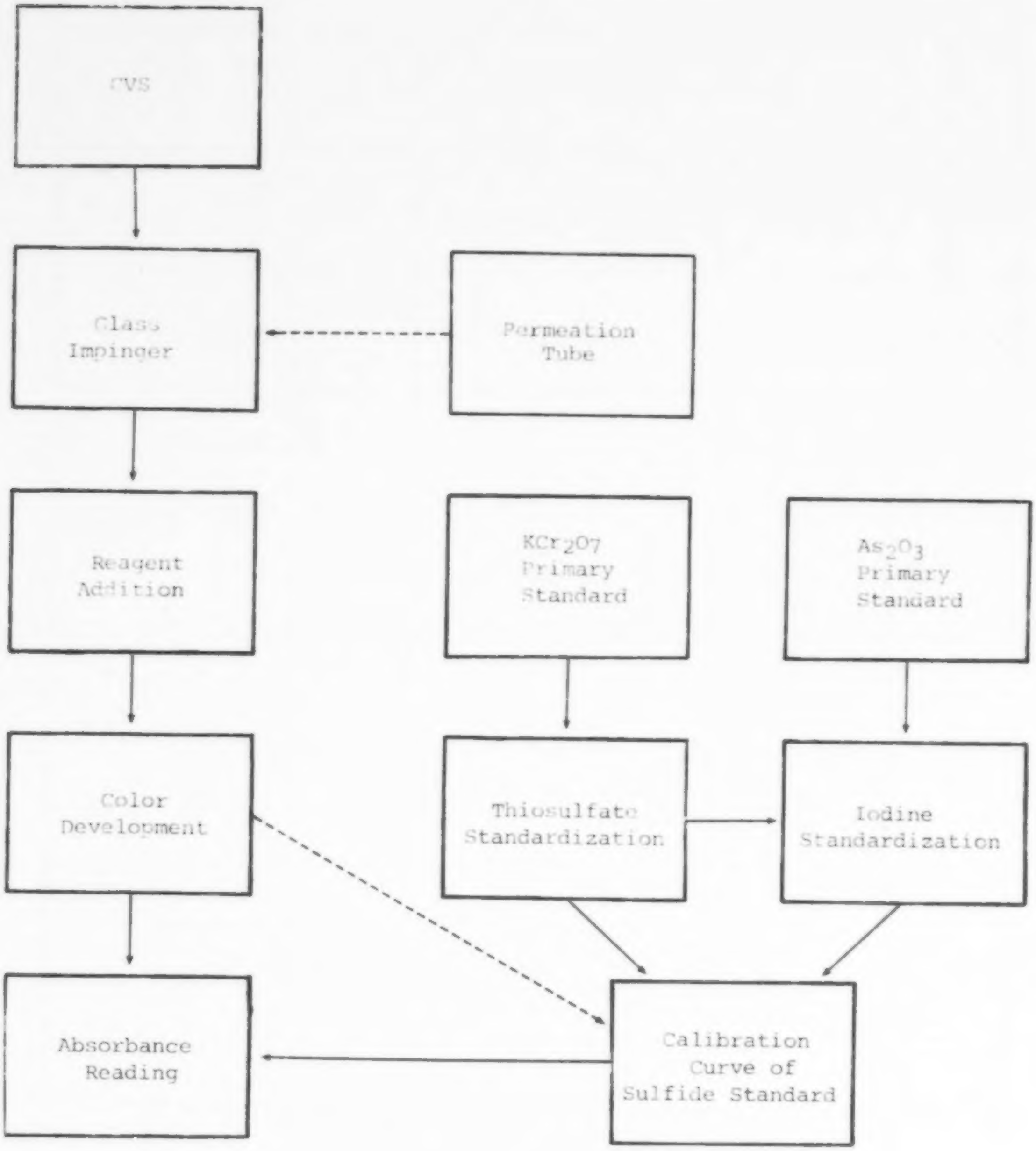

CVS
Glass Impinger
Permeation Tube
Reagent Addition
KCr_2O_7 Primary Standard
As_2O_3 Primary Standard
Color Development
Thiosulfate Standardization
Iodine Standardization
Absorbance Reading
Calibration Curve of Sulfide Standard

Figure 4. Hydrogen sulfide analysis flow schematic.

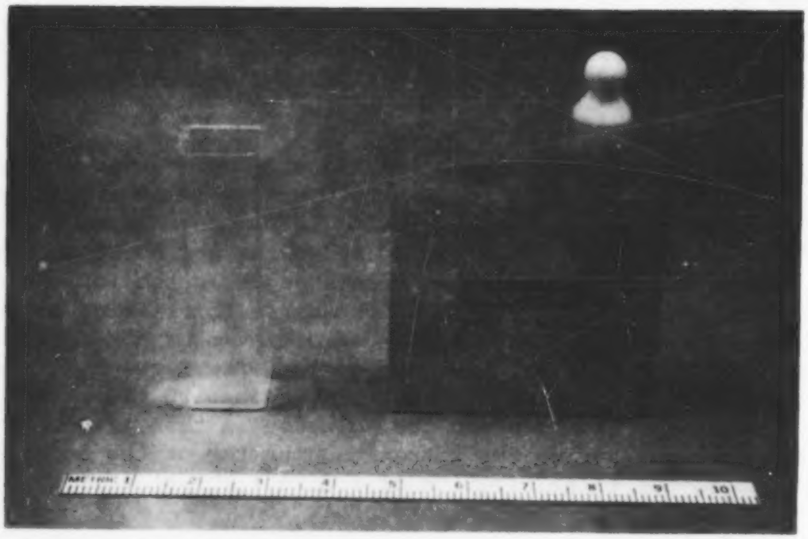
thiosulfate solution. As the end point is approached, about 5 mℓ of the starch indicator is added. The solution is blue from the starch-iodine complex before the end point is reached. At the end point, there is a change in color from blue to green due to the production of Cr (III) ion. This standardized thiosulfate solution is used to standardize the dilute iodine solution and also determine the sulfide ion concentration in the sulfide standard solution.

The concentrated iodine solution is standardized against primary standard grade arsenic trioxide by an iodimetric titration. A weighed portion of 0.15 to 0.20 g (0.001 mole) arsenic trioxide is placed into an Erlenmeyer flask. Then, 10 to 20 mℓ of 1.0 M sodium hydroxide are added to dissolve the solid. With a small piece of blue litmus paper as the indicator, 1.0 M hydrochloric acid is added dropwise until the arsenic trioxide solution is slightly acidic. About 1.0 g (0.01 mole) of sodium bicarbonate is slowly added to prevent the loss of solution due to the effervescence of carbon dioxide. The resulting solution is diluted to about 100 mℓ. About 2 mℓ of the starch indicator is added and the solution is then titrated with the 0.1 N iodine solution. During the titration, the top of the buret should be covered to minimize the volatilization of iodine. The standardization needs to be done only once for the concentrated solution.

The dilute iodine solution (0.01 N) is standardized against a previously standardized thiosulfate solution. To a beaker containing 25 mℓ of the dilute iodine solution, 10 mℓ of concentrated hydrochloric acid is added and the resulting solution is immediately titrated with the standardized thiosulfate solution. Just before the endpoint, starch is added to serve as an indicator. The filute iodine solution should be standardized daily.

The concentration of the standard sulfide solution is determined by an iodometric method. To three (3) Erlenmeyer flasks, 10 mℓ of the absorbing solution and 50 mℓ of the sulfide standard solution are added and the resulting solution is mixed. Into one of the flasks 5 mℓ of the 0.01 N iodine solution and 19 mℓ of concentrated hydrochloric acid are added. The resulting solution is immediately titrated to the starch endpoint with standardized thiosulfate solution. This procedure is then repeated for the remaining two flasks and for two blanks prepared with only the absorbing reagent and 50 mℓ of vacuum boiled, deionized water. The excess iodine in the solution is reacted with the thiosulfate and the amount of sulfide ion present can be back-calculated.

A Beer's Law curve is determined by adding 0.1, 0.25, 0.5, 1.0, 2.0, 3.0, and 5.0 mℓ of the sulfide standard solution to seven separate 100 mℓ volumetric flasks with each containing 10 mℓ of the absorbing reagent. A blank of the absorbing reagent is also prepared. A 10 mℓ portion of the amine solution is carefully poured down the side of each flask taking care not to introduce air bubbles. Then, 2 mℓ of the ferric ion solution is added and gently swirled. The contents are then diluted to 100 mℓ with vacuum boiled, deionized water and placed in the dark to develop for 30 minutes. This procedure should be repeated for the remaining flasks and the blank. The absorbance is read at 667 nm in a spectrophotometer against the reagent blank. The concentration of the samples are used to determine a best fit plot of the Beer's Law curve. In the higher concentration ranges,



One and four cm pathlength curvettes

Reading the absorbance

Figure 5. The analysis of hydrogen sulfide in exhaust.

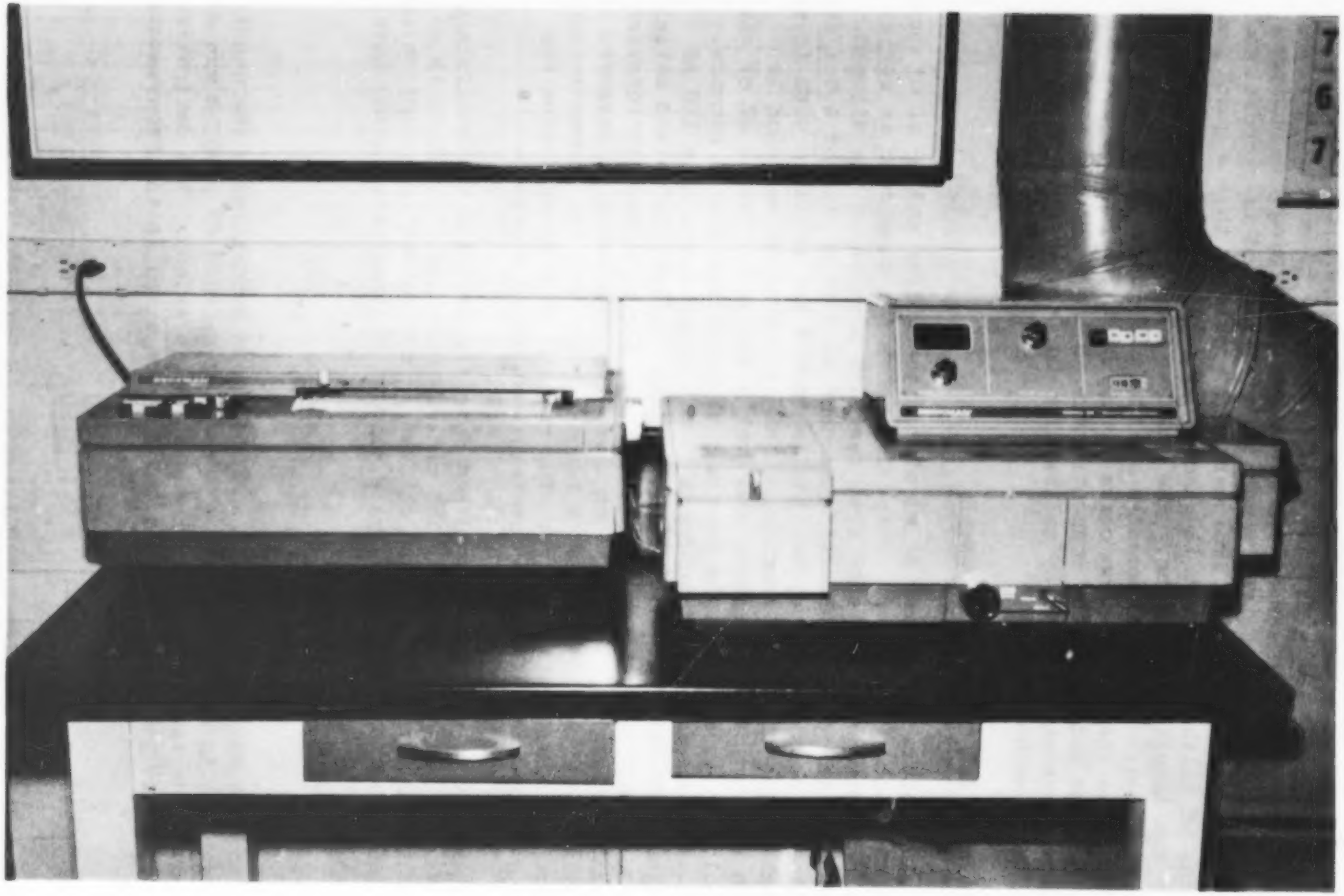


Figure 6. Beckman Model 25 spectrophotometer.

the curve is nonlinear and does not necessarily follow Beer's Law.

Another more efficient means of generating a Beer's Law curve requires the use of permeation tubes as a calibration standard. The calibration curve is generated by passing a diluent gas (preferably nitrogen) over the permeation tube and through a set of two impingers containing the buffered zinc acetate absorbing reagent. The length of time sampled is proportional to the concentration in the set of impingers. Not only is this a quick and efficient means of calibration, but it also takes into account the collection efficiency of the sampling technique. The samples are developed by the technique described above. The absorbance is read at 667 nm and this absorbance is used to determine the calibration curve. This best fit plot of the Beer's Law curve is used to determine the concentration of the samples. A quick and easy method of providing a daily calibration for the instrument can be obtained with this method.

Sample Acquisition and Color Development

To two clean glass impingers, 10 mℓ of acetate buffer and 40 mℓ of vacuum boiled, deionized water are added. These impingers are connected in series in the sampling system. During each test cycle, a portion of the diluted exhaust is bubbled through the absorbing reagent at a flow rate of 4.0 ℓ/min. Upon completion of each driving cycle, the impingers are replaced with fresh ones. To each of the collected samples, 10 mℓ of the amine solution is added through the top of the impinger and gently swirled. Then 2 mℓ of the ferric ion solution is added in the same manner and mixed for 30 seconds. The solution is quantitatively transfered from the impingers to a 100 mℓ volumetric flask and diluted to 100 mℓ with vacuum boiled, deionized water. The color development is complete in 30 minutes. The procedure is repeated with the remaining samples. After 30 minutes, the absorbance is measured on a spectrophotometer at 667 nm against a reagent blank and the concentration determined from the calibration curve. The one and four cm curvettes are shown in Figure 5 and the spectrophotometer is shown in Figure 6.

This procedure is well documented and commonly used for the analysis of hydrogen sulfide. With a 4 cm cell, the minimum detectable quantity is on the order of 0.01 ppm. Extensive wet chemistry is involved to establish the calibration curve but the sample analysis time is minimal after color development.

CALCULATIONS

This procedure has been selected and developed to determine the quantity of hydrogen sulfide in dilute exhaust. A Hewlett-Packard 65 program was designed to reduce the time required for manual calculations. The derivation of the equations are given below and a copy of the steps in the program are shown in Figure 7.

Derivation of Equation

The concentration of sulfide ion in μg/mℓ is obtained from the Beer's Law plot of the absorbance. This is the actual concentration in the impinger

HP-65 User Instructions

Title HYDROGEN SULFIDE IN µg/m^3 Page ____ of ____

Programmer E. Robert Fanick Date 8/25/78

HYDROGEN SULFIDE IN µg/m^3

STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch To On; Switch To Run				
0_2	Feed Card From Left To Right				
0_3	Initialize		f	REG	
0_4	Set Decimal Place		DSP	2	
1	Input Sample Volume	FT^3	A		$\frac{^\circ Rm^3}{"Hg}$
2	Input Barometric Pressure	"Hg	R/S		$^\circ Rm^3$
3	Input Sample Temperature	°F	R/S		$\frac{1}{m^3}$
4	Input Dilution Factor		R/S		$\frac{1}{m^3}$
5	Input Solution Volume	mℓ	R/S		$\frac{m\ell}{m^3}$
6	Input Bubbler #1 Concentration	µg/mℓ	R/S		µg/m^3
7	Output Bubbler #1 Concentration				µg/m^3
8			R/S		
9	Input Bubbler #2 Concentration	µg/mℓ	R/S		µg/m^3
10	Output Bubbler #2 Concentration				µg/m^3
11	Output Sum Total Concentration		R/S		µg/m^3
12	Output Total Concentration		R/S		ppm

Figure 7. HP-65 User Instructions.

HP-65 Program Form

Title HYDROGEN SULFIDE IN EXHAUST (2 BUBBLER CALCULATION) Page ____ of ____

SWITCH TO W/PRGM PRESS f PRGM TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23	
A	11	Input-Sample Vol., Ft^3
2	02	
÷	81	
R/S	84	Input-Barometer, "Hg
X	71	
STO 1	3301	
R/S	84	Input-Sample Temp., °F
4	04	
6	06	
0	00	
+	61	
RCL 1	3401	
÷	81	
R/S	84	Input Dilution Factor
×	71	
R/S	84	Input Abs. Soln. Vol.mℓ
×	71	
STO 2	3302	
RCL 2	3402	
R/S	84	Input Sample Conc., µg S$^=$/mℓ
×	71	Bubbler #1
1	01	
.	83	
0	00	
6	06	
3	03	
×	71	
STO 3	3303	
R/S	84	Output Sample Conc., µg H$_2$S/m^3
RCL 2	3402	Bubbler #1
R/S	84	Input Sample Conc., µg/S$^=$/mℓ
×	71	Bubbler #2
1	01	
.	83	
0	00	
6	06	
3	03	
×	71	
R/S	84	Output Sample Conc., µg H$_2$S/m^3
RCL 3	3403	Bubbler #2
+	61	
R/S	84	Output Total Conc., µg H$_2$S/m^3
0	00	
.	83	
0	00	
0	00	
0	00	
7	07	
5	05	

KEY ENTRY	CODE SHOWN	COMMENTS
0	00	
2	02	
X	71	
R/S	84	Output-PPM H$_2$S
RTN	24	

REGISTERS

R$_1$ ____

R$_2$ ____

R$_3$ ____

R$_4$ ____

R$_5$ ____

R$_6$ ____

R$_7$ ____

R$_8$ ____

R$_9$ ____

LABELS

A ____
B ____
C ____
D ____
E ____
0 ____
1 ____
2 ____
3 ____
4 ____
5 ____
6 ____
7 ____
8 ____
9 ____

FLAGS

1 ____

2 ____

Figure 7 (Cont'd). HP-65 Program Form.

and does not take into account any of the experimental parameters. The first correction is for the dilution factor and the absorbing solution volume in mℓ:

$$\underset{(\mu g/\text{sample})}{C_{sam}} = C_{ex} \times \text{D.F.} \times \text{A.S.V.}$$

where C_{sam} is the sample concentration
C_{ex} is the actual concentration in the impinger
D.F. is the dilution factor
A.S.V. is the absorbing solution volume in mℓ.

The concentration can now be expressed in $\mu g/ft^3$ and $\mu g/m^3$ by dividing by the experimental sample volume for the test:

$$\underset{(\mu g/ft^3)}{C_{sam}} = \frac{C_{ex} \times \text{D.F.} \times \text{A.S.V.}}{\text{sample volume, } ft^3}$$

A conversion factor for cubic feet to cubic meters yields:

$$\underset{(\mu g/m^3)}{C_{sam}} = \frac{C_{ex} \times \text{D.F. A.S.V.} \times 35.31\ ft^3/m^3}{\text{sample volume, } ft^3}$$

The concentration is now at the experimental conditions. The temperature and pressure are corrected to 20°C (68°F) and 760 mm Hg (29.92" Hg), respectively.

$$\underset{(\mu g/m^3)}{C_{sam}} = \frac{C_{ex} \times \text{D.F.} \times \text{A.S.B.} \times 35.31\ ft^3/m^3 \times 29.92\text{" Hg}}{\text{sample volume, } ft^3} \times \frac{(\text{sample temp. °F} + 460\text{°R})}{\text{barometric pressure, " Hg} \times 528\text{°R}}$$

This corrected concentration is then transferred to a master computer sheet for the final calculation to express the emission in mg/km.

Sample Calculations

Assume that a set of six samples was taken from dilute exhaust during several different driving cycles. The volume of dilute exhaust collected from the first test is 3.185 ft^3 in 50 mℓ of absorbing reagent at a barometric pressure of 29.41" Hg and a temperature of 77°F. The sample was diluted to 100 mℓ and allowed to develop for 30 minutes. The analysis was conducted and found to contain 14.2 $\mu g\ S^=/m\ell$. The sample calculation is shown below:

$$\underset{(\text{corrected})}{\mu g\ S^=/m^3} = \frac{14.2 \times 2 \times 50 \times 35.31 \times 29.92 \times (77 + 460)}{3.185 \times 29.41 \times 528}$$

$$\mu g\ S^=/m^3 = 16289$$

The concentration in ppm is:

$$\text{ppm } H_2S = \frac{16289\ \mu g\ S^=}{m^3} \times \frac{0.0007502\ m\ell\ S^=}{\mu g\ S^=} \times \frac{34.08\ \mu g\ H_2S}{32.06\ \mu g\ S^=}$$

$$\text{ppm } H_2S = 13.0$$

The values for the six sets of sample data are given in Figure 8 along with the data sheet. The calculations were carried out manually and with the HP-65 program. The program will be used to calculate both $\mu g\ S^=/m^3$ and ppm H_2S and to insure rapid data turnaround. The values used in these calculations were picked at random and may not represent the expected values in exhaust.

HYDROGEN SULFIDE SAMPLE COLLECTION DATA SHEET

SWRI PROJECT NO. 11-0000-000 TEST NO. 000 TEST DATE: 2/6/78 VEHICLE: SAMPLE
FUEL: EM-237 CVS NO. 8 TUNNEL SIZE 8" DRIVER: ABC MILES: 0000
SAMPLE COLLECTION BY: ERF CHEMICAL ANALYSIS BY: ERF CALCULATIONS BY: ERF
GENERAL COMMENTS:

NO.	DRIVING CYCLE	SAMPLING CONDITIONS			DILUTION FACTOR	ABSORB. REAGENT VOLUME ML	SAMPLE			
		VOLUME FT^3	B.P. "HG	TEMP. °F			ABSORB.	µg S=/ml	PPM	
1.		3.185	29.41	77	2	50	0.169	14.2	13.0	
2		2.893	29.41	80	2	50	0.723	66.5	67.3	
3		2.800	29.38	85	2	50	0.519	47.0	49.7	
4		2.805	29.43	77	2	50	1.069	100.0	103.8	
5		2.754	29.92	76	2	50	0.875	81.6	84.7	
6		2.520	29.35	90	2	50	0.772	71.1	84.4	
7										
8										
☒	☒	①	②	③	④	⑤	☒	⑥	⑧	

Figure 8. Raw data sheet for hydrogen sulfide analysis.

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APPENDIX H

TOTAL CYANIDE PROCEDURE

THE MEASUREMENT OF TOTAL CYANIDE IN EXHAUST

The measurement of total cyanide (hydrogen cyanide + cyanogen) in exhaust is accomplished by collecting the exhaust in glass impingers. The 1.0 N potassium hydroxide absorbing solution is maintained at ice bath temperature (0°C). An exhaust sample is collected continuously during the test cycle. Upon completion of the test, an aliquot of the absorbing reagent is treated with KH_2PO_4 and Chloramine-T. A portion of the resulting cyanogen chloride is injected into a gas chromatograph equipped with an electron capture detector (ECD). External CN- standards are used to quantify results. The minimum detection limit is less than 0.01 ppm for this procedure.

SAMPLING SYSTEM

Glass impingers are used to collect exhaust samples for subsequent chemical reaction with chloramine-T in a buffered solution. A flow schematic of the sample collection system is presented in Figure 1. Two glass impingers are sufficient to collect 99+% of the HCN and C_2N_2, provided the impingers are maintained at 0-5°C with an ice bath. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. The dry gas meter determines the total flow through the impingers during a given driving cycle. The sample pump should be capable of pulling a flow rate of 4 liters/minute. A drier is included to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter allows continuous monitoring of the sample flow to insure proper flow rates during the sampling. Figure 2 shows the actual sampling system used in the analysis.

LIST OF EQUIPMENT

The equipment required in this analysis is divided into two basic categories. The first category involves the sample acquisition using the glass impingers. The second category contains equipment related to the analysis of the sample once it has been obtained. The individual items in each category are listed below:

Sample Acquisition

1. Sample pump, Thomas model 106 CA18, capable of free flow capacity of 4 ℓ/min

2. Glass impingers, Ace Glass Products, catalog no. 7530-11 29/42 bottle joints, 18/7 arm joints

3. Flowmeter, Brooks Instrument Division, Model 1555, Tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/min range

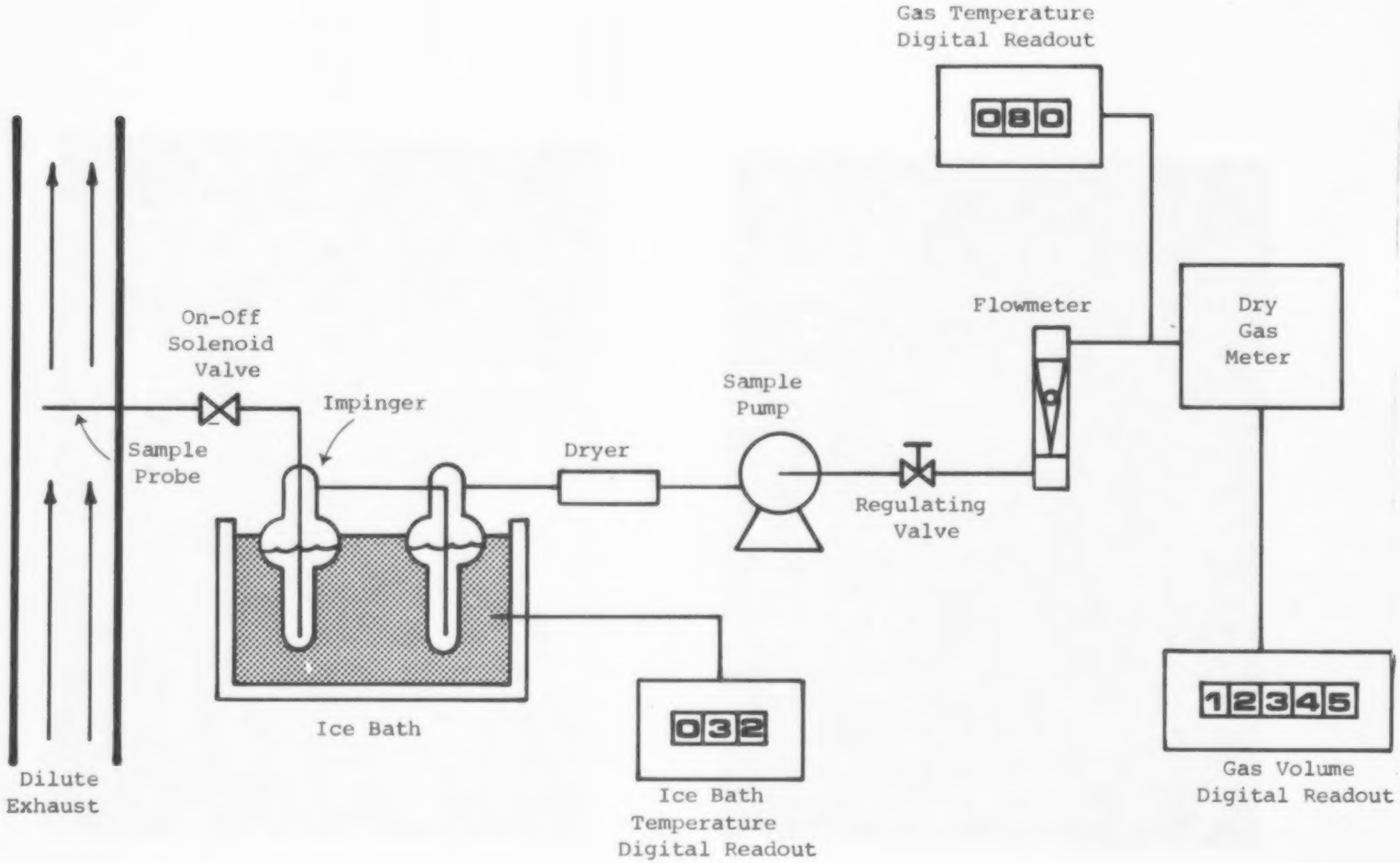
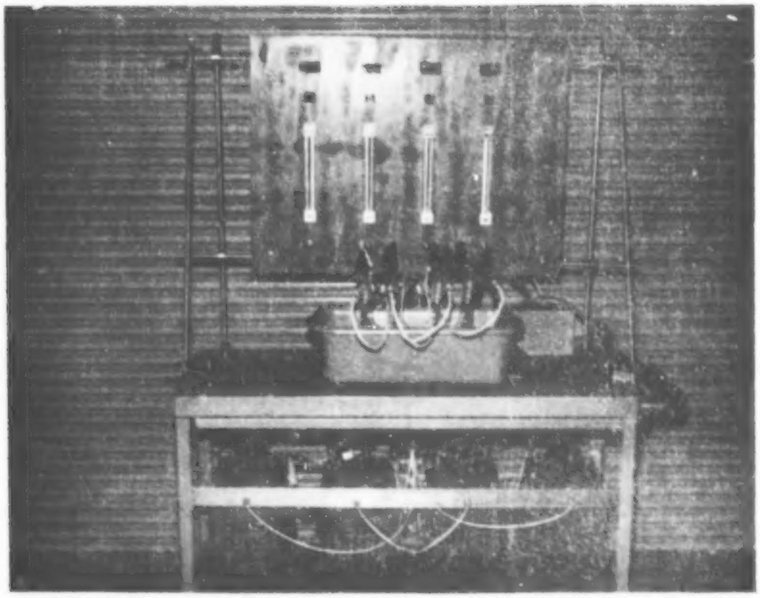
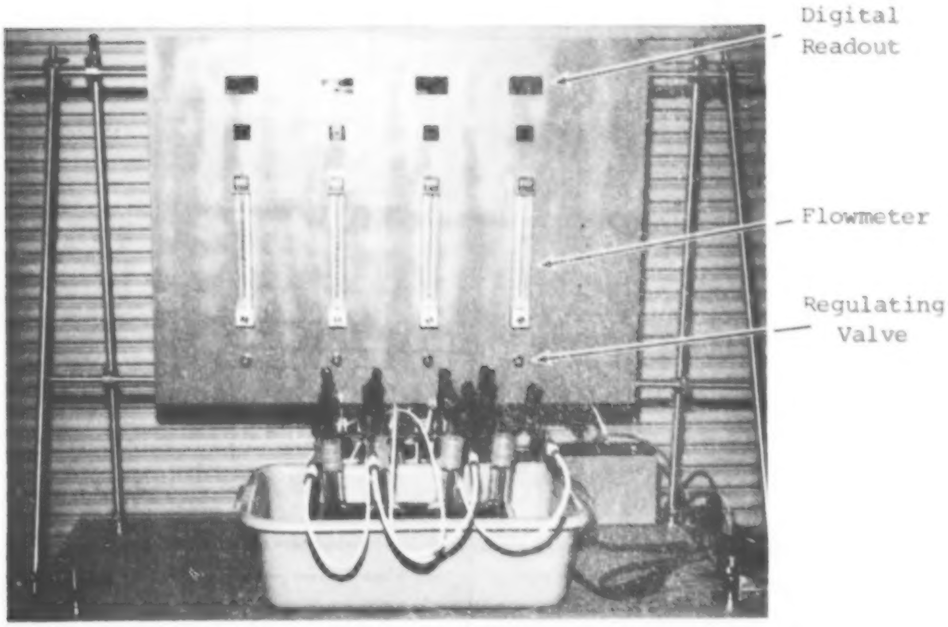

Gas Temperature Digital Readout
080
Flowmeter
Dry Gas Meter
On-Off Solenoid Valve
Impinger
Sample Pump
Dryer
Sample Probe
Regulating Valve
Ice Bath
032
12345
Dilute Exhaust
Ice Bath Temperature Digital Readout
Gas Volume Digital Readout

Figure 1. Total cyanide sample collection flow schematic.



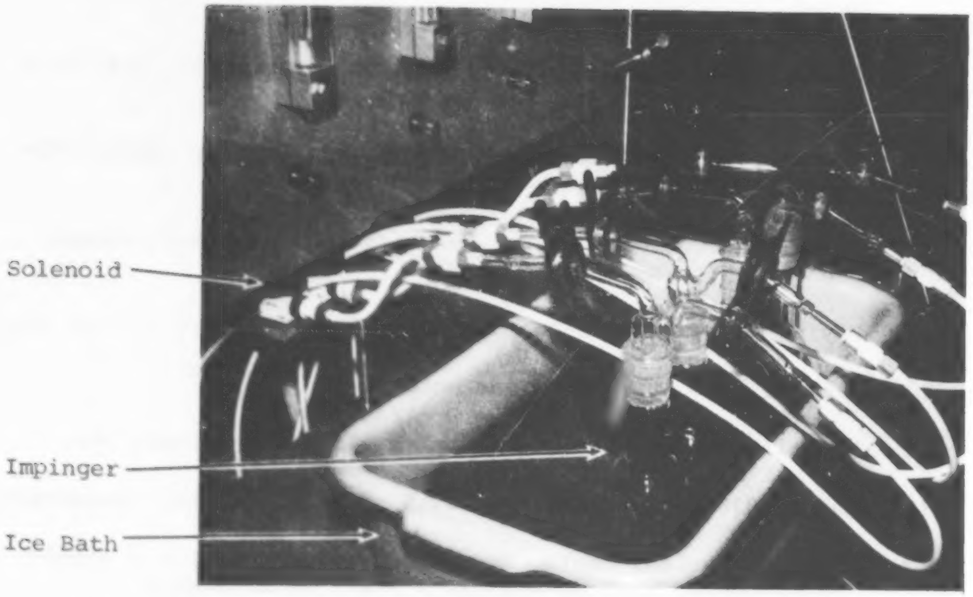
Front View



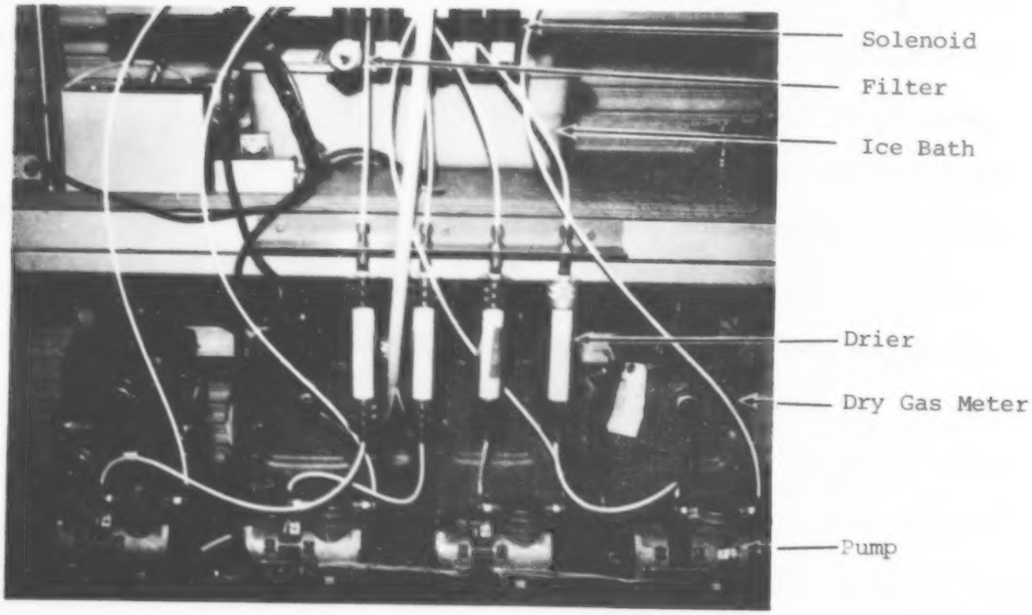
Digital Readout
Flowmeter
Regulating Valve

Close-up of Upper Front

Figure 2. Total cyanide sampling system.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). Total cyanide sampling system.

4. Regulating valve, Nupro 4MG, stainless steel

5. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity

6. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" OD x 1/8" ID

7. Teflon Solenoid Valve, The Fluorocarbon Company, Model DV2-144NCA1

8. Miscellaneous teflon nuts, ferrules, unions, tees, clamps, connectors, etc.

9. Drying tube, Nalgene Corporation, 10 cm length x 1/2 in. dia.

10. Digital readout for dry gas meter

11. Miscellaneous electrical switches, lights, wirings, etc.

12. Model 2036/J/1, Analog Device, 6 channel, digital thermometer

13. Iron/Constantan, Thermo Sensors Corporation, type J single thermocouple, 1/4" OD stainless steel metal sheath

Sample Preparation

1. Glass gas syringe, teflon tipped plunger, 100 µl, Pressure-Lok Series A-2, Alltech Associates

2. Glass Reacti-vials, 5 mℓ, Pierce Chemical Company

3. Class A, 1 mℓ volumetric pipets

4. Class A, 2 mℓ volumetric pipets

5. Class A, 25 mℓ volumetric pipets

6. Class A, 50 mℓ volumetric flask

7. Class A, 100 mℓ volumetric flask

8. Class A, 250 mℓ volumetric flask

9. Class A, 500 mℓ volumetric flask

10. Class A, 1000 mℓ volumetric flask

Instrumental Analysis

1. Perkin-Elmer Model 3920B gas chromatograph equipped with a linearized electron capture detector (ECD)

2. Soltec Model B-281 1 mv recorder

3. Hewlett-Packard Model 3354 gas chromatograph computer system with remote teletype printout

LIST OF REAGENTS

This procedure requires the sample collection in a glass impinger using 1.0 N potassium hydroxide absorbing reagent. A buffer is added to control the pH and Chloramine T is added to convert the CN- to cyanogen chloride. Potassium cyanide is used as the CN- standard in 1.0N KOH. The reagents are listed below along with the manufacturer and quality.

1. Potassium phosphate monobasic, formula weight = 136.09, chemical formula = KH_2PO_4, ACS Analytical Reagent Grade, crystals, Mallinckrodt Code 7100.

2. Potassium hydroxide, formula weight = 56.11, chemical formula = KOH, ACS Analytical Reagent Grade, pellets, Mallinckrodt Code 6984

3. Potassium cyanide, formula weight = 65.12, chemical formula KCN, ACS Analytical Reagent Grade, granular, Mallinckrodt Code 6881

4. Chloramine-T (sodium para-toluene sulfonchloramide trihydrate), formula weight = 282.70, chemical formula = $1\text{-}CH_3C_6H_4\text{-}4SO_2NClNa \cdot 3H_2O$, Assay (by titration) 96% minimum, Eastman, crystals, Eastman Code 1022

PREPARATION OF REAGENTS

Primary standard - the primary standard is prepared by dissolving 0.602 grams of KCN in 500 mℓ of 1.0 N KOH. This is equivalent to 500 ppm HCN (500 μg HCN/mℓ) or a 481 ppm CN- (481 μg CN-/mℓ). Additional standards are prepared from the primary standard. A typical dilution to prepare a 0-10 μg CN-/mℓ calibration curve is as follows:

mℓ of 481 μg CN-/mℓ Primary Standard	Final Diluent Volume, mℓ	CN- concentration, μg/CN-/mℓ
1.000 mℓ	50.0 mℓ	9.62
4.000 mℓ	250.0 mℓ	7.70
1.000 mℓ	100.0 mℓ	4.81
3.00 mℓ	500.0 mℓ	2.89
1.000 mℓ	250.0 mℓ	1.92
1.000 mℓ	500.0 mℓ	0.96

Buffer Solution - A 1.0 N KH_2PO_4 buffer solution is prepared by adding 13.609 g KH_2PO_4 to 100 mℓ of deionized H_2O. The buffer solution should be prepared daily.

Absorbing Reagent - The absorbing reagent is a 1.0N KOH solution. This solution is prepared by dissolving 56.11 grams of KOH in 1000 mℓ of deionized water. The absorbing reagent is stable for one week.

Chloramine-T - The Chloramine-T is the primary reagent responsible for converting the CN- to CNCl that is measured using a GC-ECD system. This reagent is prepared by dissolving 250 mg in 100 mℓ of deionized water. This reagent is the most critical in this procedure and should be prepared daily.

ANALYTICAL PROCEDURE

The analysis of total cyanide (HCN + C_2N_2) in automotive exhaust is accomplished with the use of an electron capture detector (ECD). This particular detector is highly sensitive to halogens and halogenated compounds. Chloramine-T (sodium para-toluene sulfonchloramide) oxidizes the cyanide ion to CN+ which in turn combines with chloride ion to form cyanogen chloride (CNCl). Total cyanide can then be analyzed by the following procedure. The analysis flow schematic for the total cyanide procedure is shown in Figure 3.

During each test cycle a portion of the diluted exhaust is bubbled through 25 mℓ of 1.0N potassium hydroxide absorbing reagent in two impingers at a flow rate of 4.0 ℓ/min. Upon completion of each driving cycle the impingers are replaced with fresh ones. A 1 mℓ aliquot is removed from one of the impingers and placed in a 5 mℓ Glass Reacti-vial. A 2 mℓ aliquot of 1.0N potassium dihydrogen phosphate buffer is then added carefully down the side of the vial. This adjusts the pH to neutral or slightly acid. A 1 mℓ aliquot of Chloramine-T is carefully added down the side of the vial to the buffered solution. Turbulent addition of this reagent can cause premature release of cyanogen chloride. The cap with a septum top is immediately screwed tightly into place. The resulting solution is then set aside for 5 minutes. This allows the Chloramine-T to react completely with the trapped cyanide ion. The vial is vibrated for 5 seconds to release cyanogen chloride into the gas phase. A 100 μℓ sample of the head space is removed through the septum top of the vial using a gas-tight glass syringe and immediately injected as a single slug into the gas chromatograph. This procedure is then repeated for the second impinger. The step-wise procedure for total cyanide analysis is shown in Figure 4.

A Perkin-Elmer 3920B gas chromatograph with an ECD is used to analyze the sample. A 6' × 1/8" stainless steel column packed with 100/120 mesh Porapak Q is employed to analyze the sample. The carrier gas is argon/5 percent methane at a flow rate of 40 mℓ/min. and the column temperature is isothermal at 140°C. In the order of elution, the peaks are oxygen, carbon dioxide, water, and cyanogen chloride. The peak area is determined with a Hewlett-Packard Model 3354 computer system with a remote teletype printout. The peak area is compared to a standard cyanide ion solution which is developed in a manner similar to that of the sample. Figure 5 shows the actual analytical system with gas chromatograph, detector, integrator, and recorder.

This procedure provides a rapid and sensitive method of analyzing HCN and C_2N_2 in exhaust without extensive wet chemical work up. The analysis time is on the order of about 5 minutes after injection into the gas

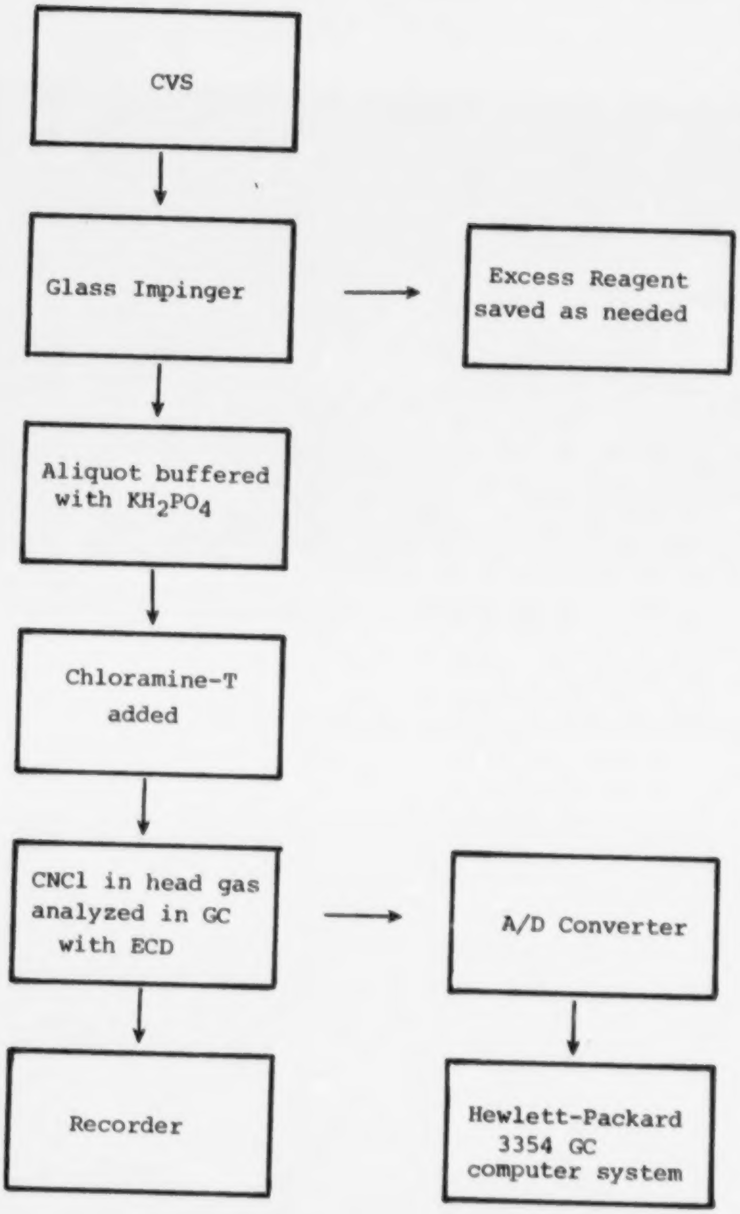
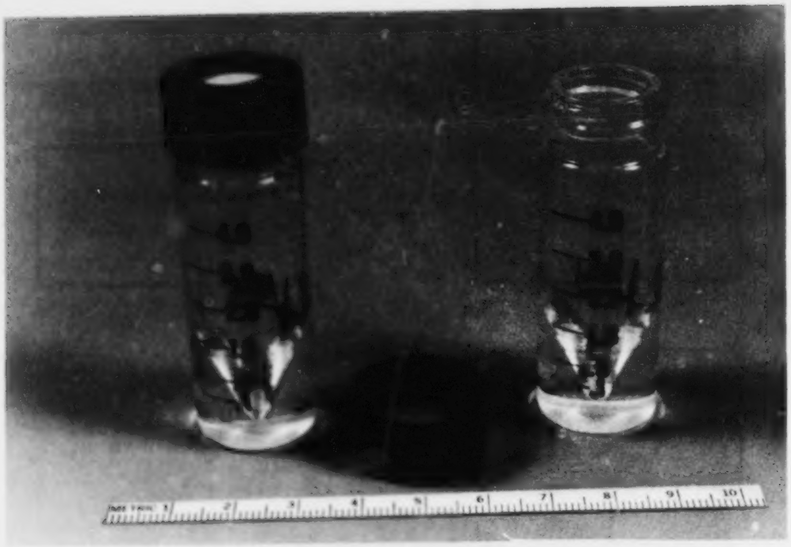
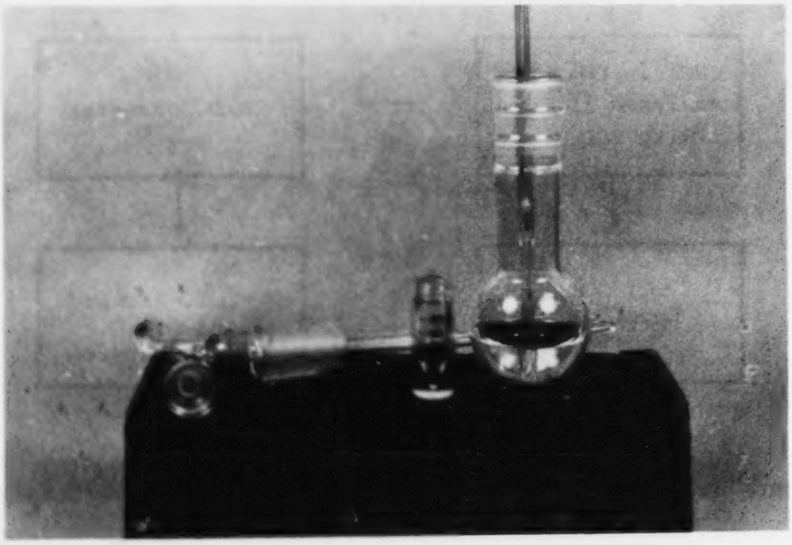

CVS
Glass Impinger
Excess Reagent saved as needed
Aliquot buffered with KH_2PO_4
Chloramine-T added
CNCl in head gas analyzed in GC with ECD
A/D Converter
Recorder
Hewlett-Packard 3354 GC computer system

Figure 3. Total Cyanide (HCN + C_2N_2) Analysis Flow Schematic.



Step 1. Glass Reacti-vial with septum cap



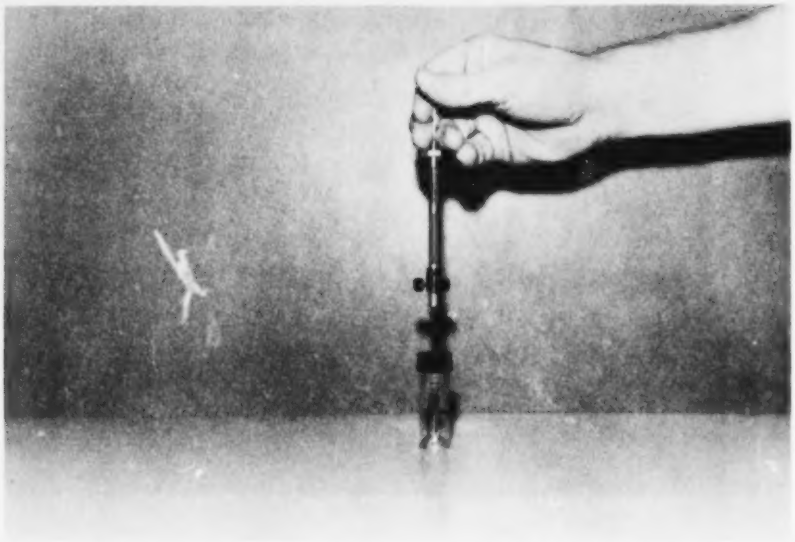
Step 2. Aliquot removal

Figure 4. Various steps in sample collection and analysis of total cyanide in exhaust.

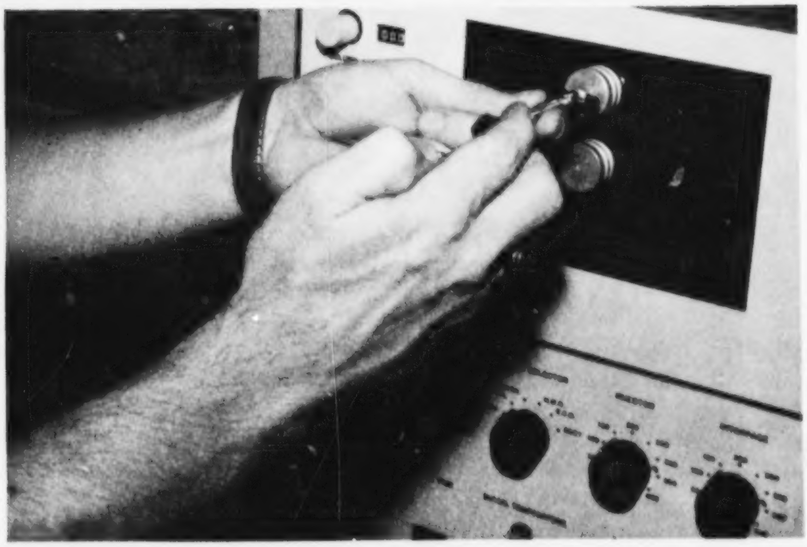
Step 3. Reagent addition

Step 4. Sample shaking

Figure 4 (Cont'd). Various steps in sample collection and analysis of total cyanide in exhaust.



Step 5. Head gas removal



Step 6. Sample injection

Figure 4 (Cont'd). Various steps in sample collection and analysis of total cyanide in exhaust.

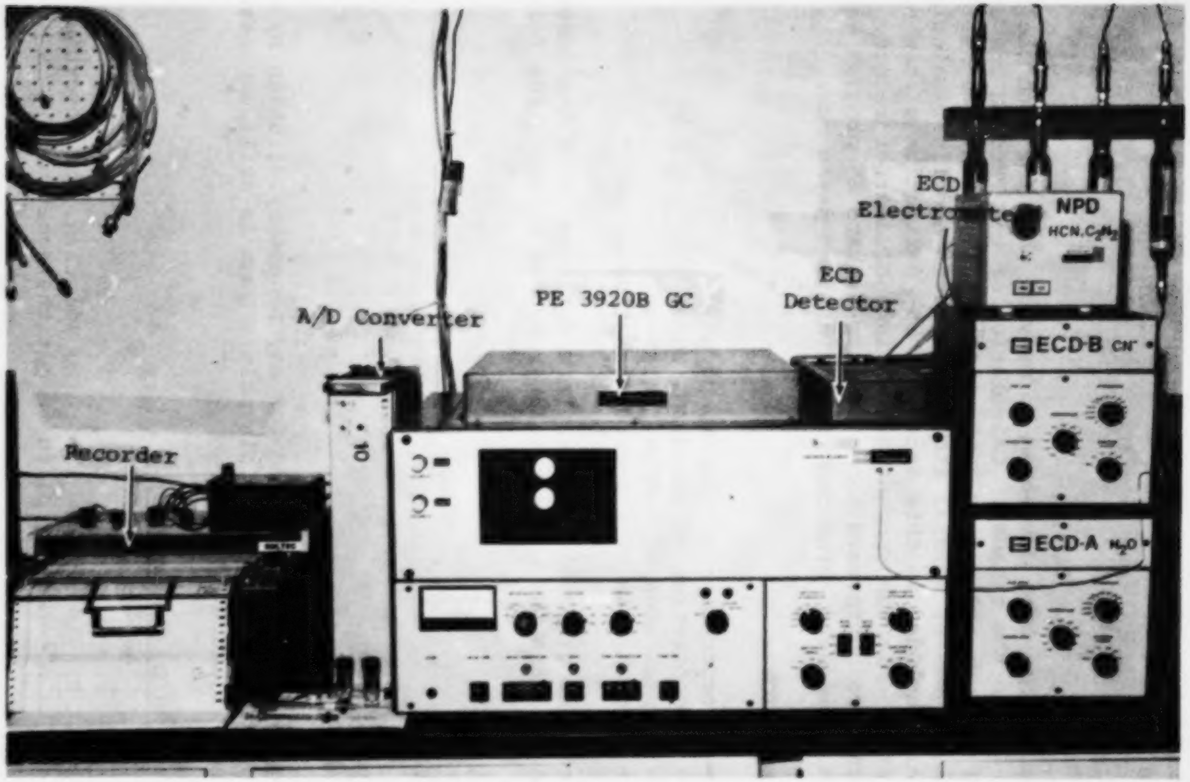

Recorder
A/D Converter
10
PE 3920B GC
ECD Detector
ECD Electrometer
NPD HCN.C_2N_2
ECD-B CN⁻
ECD-A N_2O

Figure 5. Total cyanide analytical system.

chromatograph. The sensitivity of the ECD extends the minimum detectable limit to less than 0.01 ppm cyanide ion with the specified flow rates, absorbing solution volume, syringe size, vial size, and reagent quantities. This limit can possibly be extended by changing these parameters. The simplicity and rapid data turnover makes this procedure ideal for repetitive analysis. A gas chromatograph trace for total cyanide in dilute gasoline exhaust is shown in Figure 6 and a chromatogram for the cyanide standard is shown in Figure 7.

CALCULATIONS

This procedure has been developed to provide the user with the as-measured total CN- in the exhaust. Calculation of the results are expressed in μg CN-/m^3 of exhaust and ppm CN-. In order to allow implementation of this analytical procedure, several items related to the final calculation of total cyanide are included in this section. The derivation of the equation used in calculating emission concentrations is included for record. The basic calculations are straightforward and a Hewlett-Packard 65 program was developed to provide rapid data turnaround during a given day's run.

DERIVATION OF EQUATION

Let Csam = concentration of sample, μg/mℓ
Cstd = concentration of standard, μg/mℓ
Asam = GC peak area of sample, relative units
Astd = GC peak area of standard, relative units

Since the gas chromatograph electron capture detector (ECD) has demonstrated a linear response in the CN- concentration range of concern, the following equation holds true:

$$\frac{\text{Csam}}{\text{Asam}} = \frac{\text{Cstd}}{\text{Astd}}$$

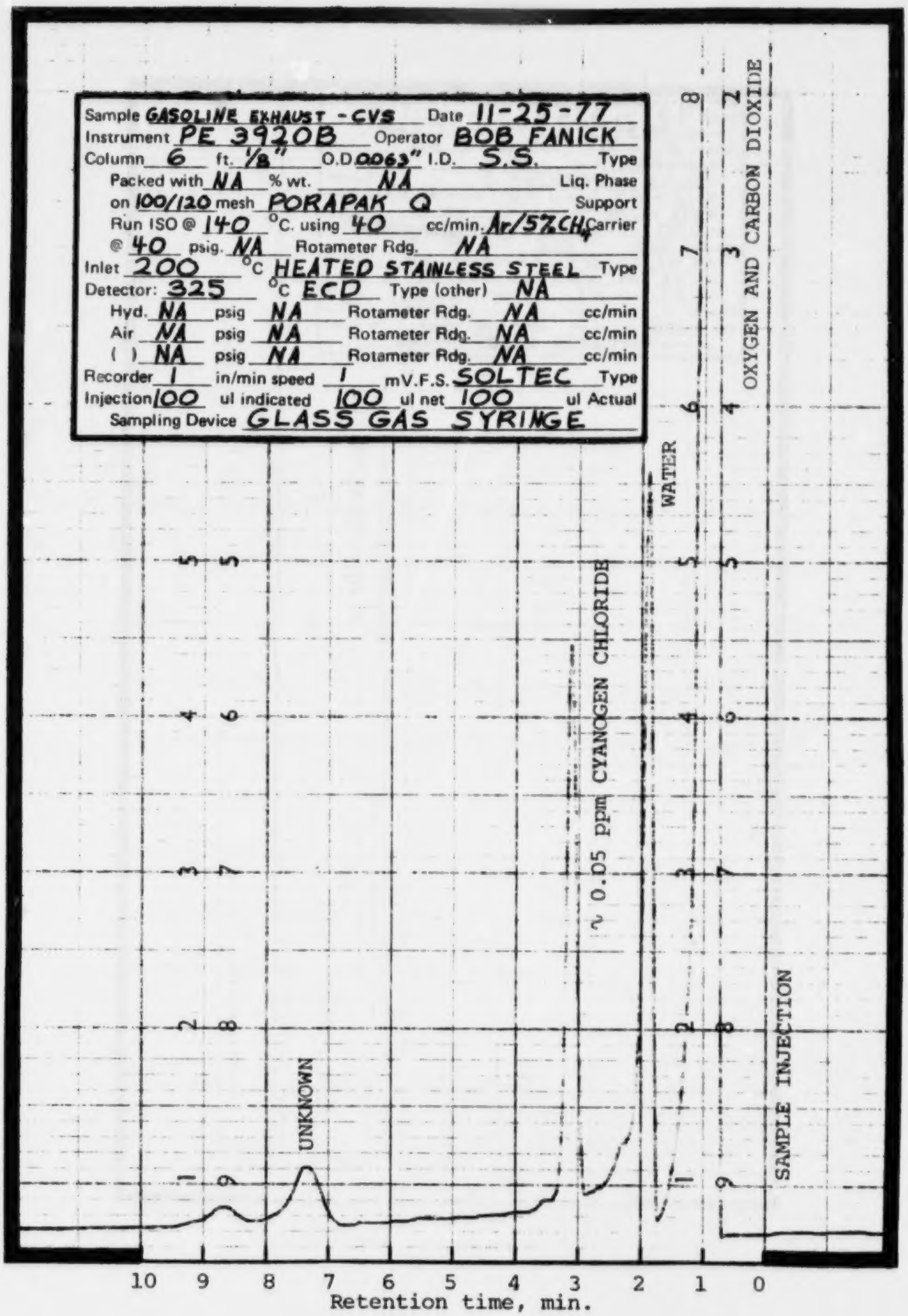
$$\text{Csam} = \frac{\text{Cstd x Asam}}{\text{Astd}}$$

The Csam in the solution is corrected for any necessary dilution by multiplying by the dilution factor. At this point, Csam is still expressed in μg CN-/mℓ absorbing reagent.

$$\text{Csam} = \frac{\text{Cstd, }\mu\text{g/m}\ell\text{ x Asam x D.F.}}{\text{Astd}}$$

To obtain the total cyanide in the absorbing solution, the absorbing reagent volume (expressed in mℓ) is multiplied to get the equation:

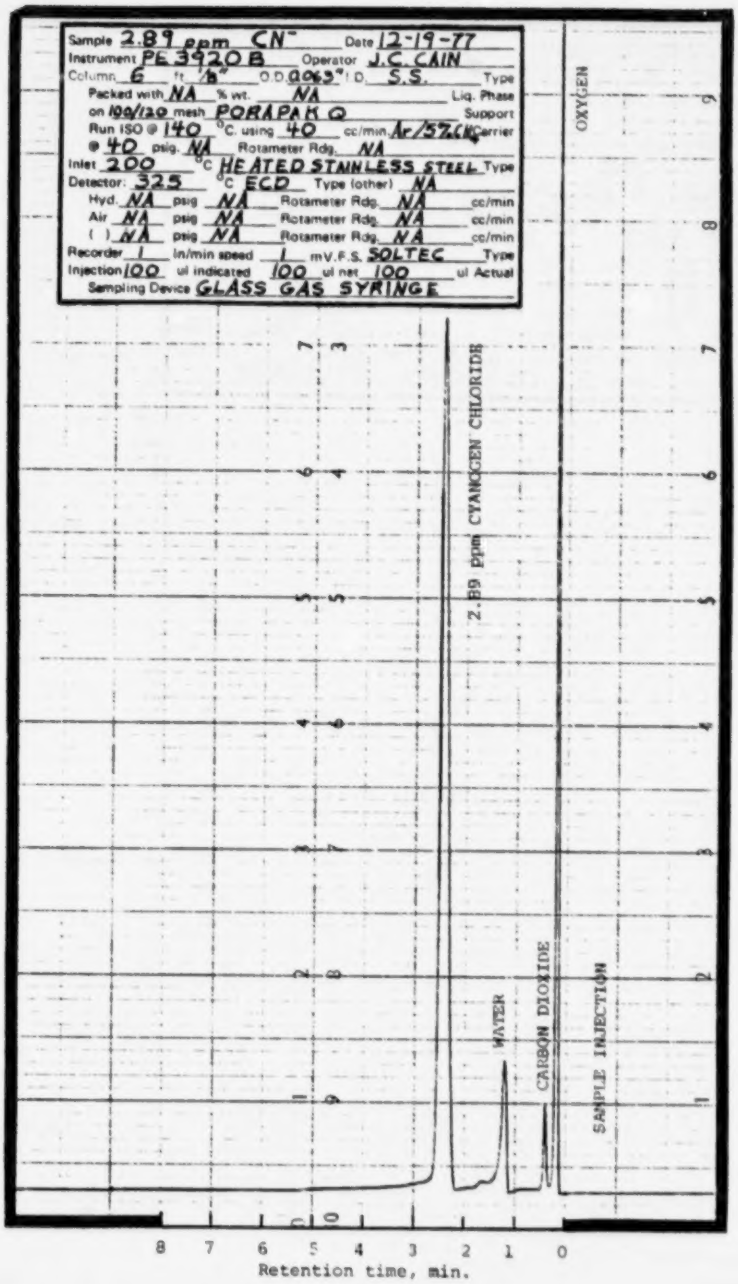
$$\underset{(\mu\text{g/ft}^3)}{\text{Csam}} = \frac{\text{Cstd, }\mu\text{g/m}\ell\text{ x Asam x D.F. x Abs. vol, m}\ell}{\text{Astd}}$$



Sample GASOLINE EXHAUST - CVS Date 11-25-77
Instrument PE 3920B Operator BOB FANICK
Column 6 ft. 1/8" O.D .0063" I.D. S.S. Type
Packed with NA % wt. NA Liq. Phase
on 100/120 mesh PORAPAK Q Support
Run ISO @ 140 °C. using 40 cc/min. Ar/5% CH_4 Carrier
@ 40 psig. NA Rotameter Rdg. NA
Inlet 200 °C HEATED STAINLESS STEEL Type
Detector: 325 °C ECD Type (other) NA
Hyd. NA psig NA Rotameter Rdg. NA cc/min
Air NA psig NA Rotameter Rdg. NA cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 in/min speed 1 mV.F.S. SOLTEC Type
Injection 100 ul indicated 100 ul net 100 ul Actual
Sampling Device GLASS GAS SYRINGE

OXYGEN AND CARBON DIOXIDE
WATER
∿ 0.05 ppm CYANOGEN CHLORIDE
UNKNOWN
SAMPLE INJECTION
10
9
8
7
6
5
4
3
2
1
0
Retention time, min.

Figure 6. Typical gasoline CVS-exhaust sample.



Sample 2.89 ppm CN⁻ Date 12-19-77
Instrument PE 3920 B Operator J.C. CAIN
Column 6 ft 1/8" O.D. 0.063" I.D. S.S. Type
Packed with NA % wt. NA Liq. Phase
on 100/120 mesh PORAPAK Q Support
Run ISO @ 140 °C. using 40 cc/min. Ar/5% CH_4 Carrier
@ 40 psig. NA Rotameter Rdg. NA
Inlet 200 °C HEATED STAINLESS STEEL Type
Detector: 325 °C ECD Type (other) NA
Hyd. NA psig NA Rotameter Rdg. NA cc/min
Air NA psig NA Rotameter Rdg. NA cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 in/min speed 1 mV.F.S. SOLTEC Type
Injection 100 ul indicated 100 ul net 100 ul Actual
Sampling Device GLASS GAS SYRINGE

OXYGEN
2.89 ppm CYANOGEN CHLORIDE
WATER
CARBON DIOXIDE
SAMPLE INJECTION
8
7
6
5
4
3
2
1
0
Retention time, min.

Figure 7. Typical Trace for a Standard.

The next step is to convert the sample concentration to μg per volume expressed in cubic meters. The sample acquisition is effected using dry gas meters that have units expressed in cubic feet. To make this conversion, the following steps are observed.

$$\underset{(\mu g/ft^3)}{\text{Csam}} = \frac{\text{Cstd, } \mu g/m\ell \text{ x Asam x D.F. x Abs. vol., } m\ell}{\text{Astd x Sam. Vol., } ft^3}$$

$$\underset{(\mu g/m^3)}{\text{Csam}} = \frac{\text{Cstd, } g/m\ell \text{ x Asam x D.F. x Abs. vol., } m\ell \text{ x } 35.31\ ft^3}{\text{Astd x Sam. Vol., } ft^3 \text{ x } 1\ m^3}$$

The sample volume was measured at the actual conditions of the test and is corrected to 20°C (68°F) and 760 mm Hg (29.92 Hg)

$$\underset{(\mu g/m^3)}{\text{Csam}} = \frac{\text{Cstd, } \mu g/m\ell \times \text{Asam} \times \text{D.F.} \times \text{Abs. vol., } m\ell}{\text{Astd} \times \text{sam. vol., } ft^3 \times 1\ m^3 \times \text{B.P.,"Hg}}$$

$$\times \frac{35.31\ ft^3 \times 29.92\text{"Hg} \times \text{sample temp °F} + 460\text{°R}}{528\text{°R}}$$

At this point, the concentration of the sample is expressed in $\mu g/m^3$ at 20°C (68°F) and 760 mm Hg (29.92" Hg). This concentration is then transferred to a master computer sheet for the final calculations to express the total CN-- emission rate in mg/km.

Hewlett-Packard 65 Calculations

In order to insure maximum data turnaround in a minimum time period, a Hewlett-Packard 65 program was prepared to calculate CN- concentrations from the raw data. This program is presented in Figure 8 and will be used to calculate μg CN-/m^3 and ppm CN- (as HCN). The data sheet used in the sample acquisition is also used in calculating the total CN- and ppm CN- (as HCN) concentrations.

Sample Calculations

Assume exhaust samples were collected in glass impingers for each portion of a three-bag 1975 FTP. The raw data for these tests is presented in Figure 9. Calculations were performed using the HP-65 program and manual calculations. The results of the first bag calculations are summarized below:

Cold start (505 seconds) Manual Calculations

$$\mu g\ \text{CN-}/m^3 = \frac{\text{Cstd, } \mu g/m\ell \text{ x Asam x D.F. x Abs. vol., } m\ell \text{ x } 35.31\ ft^3}{\text{Astd x sam. vol., } ft^3}$$

$$\times \frac{29.92\text{"Hg x (samp.Temp., °F + 460°R)}}{1\ m^3 \text{ x B.P., "Hg x 528°R}}$$

$$\mu g\ CN-/m^3 = \frac{(5.0)\ (1500)\ (1)\ (25)\ (35.31)\ (29.92)\ (75 + 460)}{(2000)\ (3.286)\ (1)\ (29.52)\ (528)} =$$

$$1035\ \mu g\ CN-/m^3$$

$$ppm\ CH- = \frac{\mu g\ CN-}{m^3} \times \frac{0.000859}{1\ \mu g\ CN-} \times \frac{27.026\ \mu g\ HCN}{26.018\ \mu g\ CN-}$$

$$ppm\ CN- = \frac{(1035)\ (0.00859)\ (27.026)}{(26.018)} = 0.92\ ppm\ HCN$$

Cold Start (505 seconds) HP-65 Results

μg CN-/m^3 = 1035 μg CN-/m^3

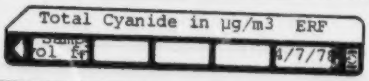
ppm CN- = 0.92 ppm
(as NCH)

Note: The values used in these calculations are picked from a range of temperatures, standards, dilution factors, etc. to validate the calculations and may not be representative of expected raw data in all cases. These calculations are presented to confirm that manual and HP-65 calculations give the same results. This was confirmed on six sets of calculations.

HP-65 User Instructions

Title Total Cyanide in $\mu g/m^3$ Page 1 of 1

Programmer E. Robert Fanick Date 4/7/78



STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to On; Switch to Run				
0_2	Feed Card from Left to Right				
0_3	Initialize		f	Reg	
0_4	Set Decimal Place		Dsp	2	
1	Input Sample Volume	ft^3	A		$\frac{°R\ m^3}{"Hg}$
2	Input Barometric	" Hg	R/S		$°R\ m^3$
3	Input Sample Temperature	°F	R/S		$\frac{1}{m^3}$
4	Input Dilution Factor		R/S		$\frac{1}{m^3}$
5	Input Solution Volume	mℓ	R/S		$\frac{m\ell}{m^3}$
6	Input Standard Concentration	µg/mℓ	R/S		$\frac{\mu g}{m^3}$
7	Input Standard Area	counts	R/S		$\frac{\mu g}{m^3\ counts}$
8	Input Sample Area Bubbler #1	counts	R/S		
9	Output Bubbler #1 Conc.		R/S		$\frac{\mu g}{m^3}$
10	Input Standard Area	counts	R/S		$\frac{\mu g}{m^3\ counts}$
11	Input Sample Area Bubbler #2	counts	R/S		
12	Output Bubbler #2 Conc.		R/S		$\frac{\mu g}{m^3}$
13	Output Total Conc.		R/S		$\frac{\mu g}{m^3}$
14	Output Total ppm HCN				ppm HCN
			CL X		
			RTN		
			f	Reg	

Figure 8. HP-65 program form.

HP-65 Program Form

Title Total Cyanide in μg/m^3 Page ____ of ____

SWITCH TO W/PRGM PRESS f PRGM TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23	
A	11	Input Sample Volume
2	02	
÷	81	
R/S	84	Input Barometric
X	71	
STO 1	3301	
R/S	84	Input Temperature
4	04	
6	06	
0	00	
+	61	
RCL 1	3401	
÷	81	
R/S	84	Input Dilution Factor
X	71	
R/S	84	Input Solution Vol.
X	71	
R/S	84	Input Stand. Conc. μg/m^3
X	71	
STO 2	3302	
RCL 2	3402	
R/S	8[illegible]	Input Std. Area
÷	81	
R/S	84	Input Samp. Area
X	71	Bubbler #1
STO 3	3303	Output Samp. Conc.
R/S	84	Bubbler #1 μg/m^3
RCL 2	3402	
R/S	84	Input Std. Area
÷	81	
R/S	84	Input Samp. Area
X	71	Bubbler #2
R/S	84	Output Samp. Conc.
RCL 3	3403	Bubbler #2 μg/m^3
+	61	
R/S	84	Total Conc. μg/m^3
0	00	
.	83	
0	00	
0	00	
0	00	
9	09	
2	02	
5	05	
X	71	
1	01	
.	83	
0	00	
3	03	

KEY ENTRY	CODE SHOWN	COMMENTS
8	08	
7	07	
X	71	
R/S	84	Output ppm HCN
RTN	24	
g NOP	3501	
g NOP	3501	

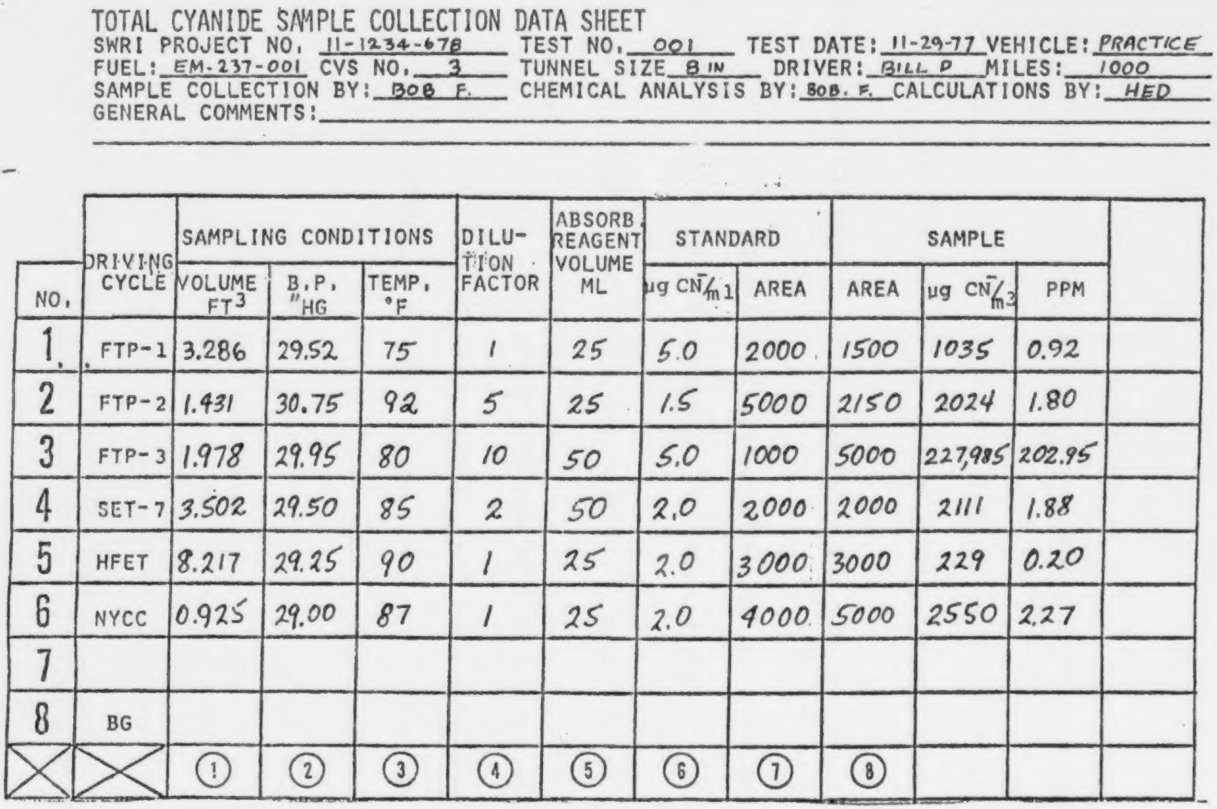
REGISTERS	
R_1	Samp.Vol. X Baro. (°R m^3)
R_2	Constant for Calc.
R_3	Samp. Conc.μg/m^3 Bubbler #1
R_4	
R_5	
R_6	
R_7	
R_8	
R_9	

LABELS	
A	Samp. Vol
B	
C	
D	
E	
0	
1	
2	
3	
4	
5	
6	
7	
8	
9	

FLAGS	
1	
2	

TO RECORD PROGRAM INSERT MAGNETIC CARD WITH SWITCH SET AT W/PRGM

Figure 8 (Cont'd). HP-65 Program Form.



TOTAL CYANIDE SAMPLE COLLECTION DATA SHEET
SWRI PROJECT NO. 11-1234-678 TEST NO. 001 TEST DATE: 11-29-77 VEHICLE: PRACTICE
FUEL: EM-237-001 CVS NO. 3 TUNNEL SIZE 8 IN DRIVER: BILL P MILES: 1000
SAMPLE COLLECTION BY: BOB F. CHEMICAL ANALYSIS BY: BOB. F. CALCULATIONS BY: HED
GENERAL COMMENTS:

NO.	DRIVING CYCLE	SAMPLING CONDITIONS			DILUTION FACTOR	ABSORB. REAGENT VOLUME ML	STANDARD		SAMPLE			
		VOLUME FT^3	B.P. "HG	TEMP. °F			µg CN$^-$/ml	AREA	AREA	µg CN$^-$/m^3	PPM	
1.	FTP-1	3.286	29.52	75	1	25	5.0	2000	1500	1035	0.92	
2	FTP-2	1.431	30.75	92	5	25	1.5	5000	2150	2024	1.80	
3	FTP-3	1.978	29.95	80	10	50	5.0	1000	5000	227,985	202.95	
4	SET-7	3.502	29.50	85	2	50	2.0	2000	2000	2111	1.88	
5	HFET	8.217	29.25	90	1	25	2.0	3000	3000	229	0.20	
6	NYCC	0.925	29.00	87	1	25	2.0	4000	5000	2550	2.27	
7												
8	BG											
☒	☒	①	②	③	④	⑤	⑥	⑦	⑧			

Figure 9. Raw data sheet for total cyanide.

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APPENDIX I

ORGANIC SULFIDE PROCEDURE

THE MEASUREMENT OF ORGANIC SULFIDES IN EXHAUST

The measurement of organic sulfides; carbonyl sulfide (COS), methyl sulfide (dimethylsulfide, $(CH_3)_2S$), ethyl sulfide (diethylsulfide, $(C_2H_5)_2S$) and methyl disulfide (dimethyldisulfide, $(CH_3)_2S_2$) in exhaust is accomplished by passing the exhaust through Tenax GC traps at -76°C. The organic sulfides are removed from the exhaust by the traps at this temperature. The exhaust sample is collected continuously during the test cycle. Thr organic sulfides are thermally desorbed from the traps into a gas chromatograph sampling system and injected into a gas chromatograph equipped with a flame photometric detector for analysis. External organic sulfide standards generated from permeation tubes are used to quantify the results. Detection limits are on the order of 0.1 ppb.

LIST OF EQUIPMENT

The analysis for the organic sulfides is performed using a gas chromatograph equipped with a flame photometric detector. The gas chromatograph, control console, sample collection, trap conditioning and trap preparation are the basic functions in the analysis. The major equipment required for each function is listed below.

Gas chromatograph and control console

1. Perkin-Elmer Model 3920B gas chromatograph equipped with a linearized flame photometric detector (FPD) and subambient temperature programmer.

2. Soltec dual channel recorder, Model B-281, 1 mv recorder.

3. Hewlett-Packard Model 3354 GC computer system with remote teletype printout.

4. Hewlett-Packard Model 1865A A/D converter.

5. Metronix Dynacalibrator Model 220-R for generation of organic sulfide standards.

6. Bendix valve oven.

7. Lindberg Furnace/Heavy Duty Model 55035.

8. Seiscor valve - gas sampling configuration.

9. Seiscor valve - backflush configuration.

10. ATC timers, Model 325A346A10PX (2 ea.).

11. Analytical column, 6' x 1/8" Teflon, 60/80 Tenax-GC.

12. ASCO solenoid valve, Model 834501 (2 ea.).

13. Brook flowmeter, R-2-15-A w/ss float, 0-150 scale.

14. Metal Bellows MB-158 pump.

15. Female quick-connect, stainless steel.

16. Nupro Model 2M stainless steel regulating valve.

17. Miscellaneous stainless steel, copper and Teflon tubing (1/8" and 1/6").

18. Miscellaneous stainless steel and brass unions, tees, etc.

19. Bud Classic II control console cabinet.

20. Miscellaneous electrical on-off switches.

Sampling

1. Perma Pure drier, Model PD 625 12S (17").

2. Brooks flowmeter, R-2-15-AA, sapphire float, 0-150 scale.

3. Metal Bellows MB-158 pump.

4. Tenax-GC trap.

5. Sodium bicarbonate trap.

6. Miscellaneous stainless steel and Teflon tubing (1/16", 1/8" and 1/4").

7. Miniature stainless steel Swagelok female quick-connects.

8. Miniature stainless steel Swagelok male quick-connects.

9. Miscellaneous stainless steel and brass unions, tees, etc.

10. Stainless steel 7.0 cm flip-top filter.

11. Reeve Angel Type AH 7.0 cm fiber glass filters.

12. Nupro Model 4M stainless steel regulating valve.

13. Dewar flask, 1 quart capacity.

Trap Preparation and Conditioning System

1. Lindberg Furnace/Heavy Duty Model 55035.
2. Brooks flowmeter, R-2-15-A, glass float, 0-150 scale.
3. Nupro Model 4M brass regulating valve.
4. Swagelok 3/8" × 1/8" stainless steel reducing unions (2 per trap).
5. Stainless steel fritted discs, 50μ, 3/8" OD (2 per trap).
6. Stainless steel tubing, 2" × 3/8" OD (0.028" wall) (1 per trap).
7. Tenax-GC, 60/80 mesh (about 1 gram per trap).
8. Miscellaneous stainless steel and Teflon tubing (1/8" and 1/4").
9. Miscellaneous stainless steel and brass unions, tees, etc.
10. Asbestos gloves, pair.
11. Refillable plexiglass gas drier, 6".
12. Nupro in-line filter, brass, Model 4.

Expendables

1. Zero hydrogen gas (GC).
2. Zero air (GC).
3. Zero helium carrier gas (GC).
4. Nitrogen (Perma Pure drier).
5. Isopropyl alcohol, $CH_3CHOHCH_3$.
6. Sodium bicarbonate.
7. Dry ice.
8. Zero nitrogen (permeation system).

CONTROL SYSTEM

A control system was developed to systematically control the flow of the two Seiscor valves. This control is accomplished by ATC electric timers and ASCO electric solenoid valves. This system employs one Seiscor valve in a gas sampling valve (GSV) configuration with the second Seiscor valve in a backflush configuration. These valves are pneumatically operated and electrically controlled. The electrical schematic for the control of the Seiscor valves using the ATC timers and ASCO electric solenoid valves is shown in Figure 1. The flow schematic for vacuum and pressure lines to the Seiscor valve are presented in Figures 2-6. The Seiscor valves have been found to operate much more dependably if a vacuum assist is included in the valve actuation controls.

SAMPLING SYSTEM

A Tenax GC trap is used to collect exhaust samples for the analysis of the organic sulfides. A flow schematic of the sample collection system is shown in Figure 7. The trap collects 99+ percent of the sulfides at flows up to 130 mℓ/min. Several views of the sampling system are shown in Figure 8. The various components of the sampling system and their functions are listed below.

Item	Component	Description
1	$NaHCO_3$ trap	2" × 3/8" OD × 0.035" wall stainless steel cartridge packed with 5 percent $NaHCO_3$ on 45/60 mesh Chromosorb P (this trap removes any H_2S or SO_2 in the exhaust sample).
2	Tenax-GC trap	2" × 3/8" OD × 0.035" eall stainless steel cartridge packed with preconditioned 60/80 mesh Tenax-GC (this trap collects and concentrates the organic sulfides).
3	Perma-Pure Drier	Model PD-625 12S Perma-Pure Drier (this dryer removes the moisture in the exhaust without jeopardizing the sample integrity).
4	Sample Pump	Model MB-158 Metal Bellows Vacuum/Compressor Pump. The sample pump pulls the exhaust sample through flip-top filter and Perma-Pure Drier and forces the sample under pressure through the remainder of the system.
5	Low temp bath	A constant low temperature bath is obtained by using a CO_2-isopropyl alcohol slurry. A bath temperature of -76 to -78°C is obtained with this bath.
6	Flip-top filter	A 7.0 cm stainless steel flip-top filter is included to remove all particulate from the exhaust sample prior to its entry into the Perma-Pure Drier.
7.	Regulating valve	A Nupro SS-4MG regulating needle valve is used to control the exhaust flow through the $NaHCO_3$ and Tenax-GC traps.
8.	Flowmeter	A Brooks Model 1550 flowmeter with R-2-15-C

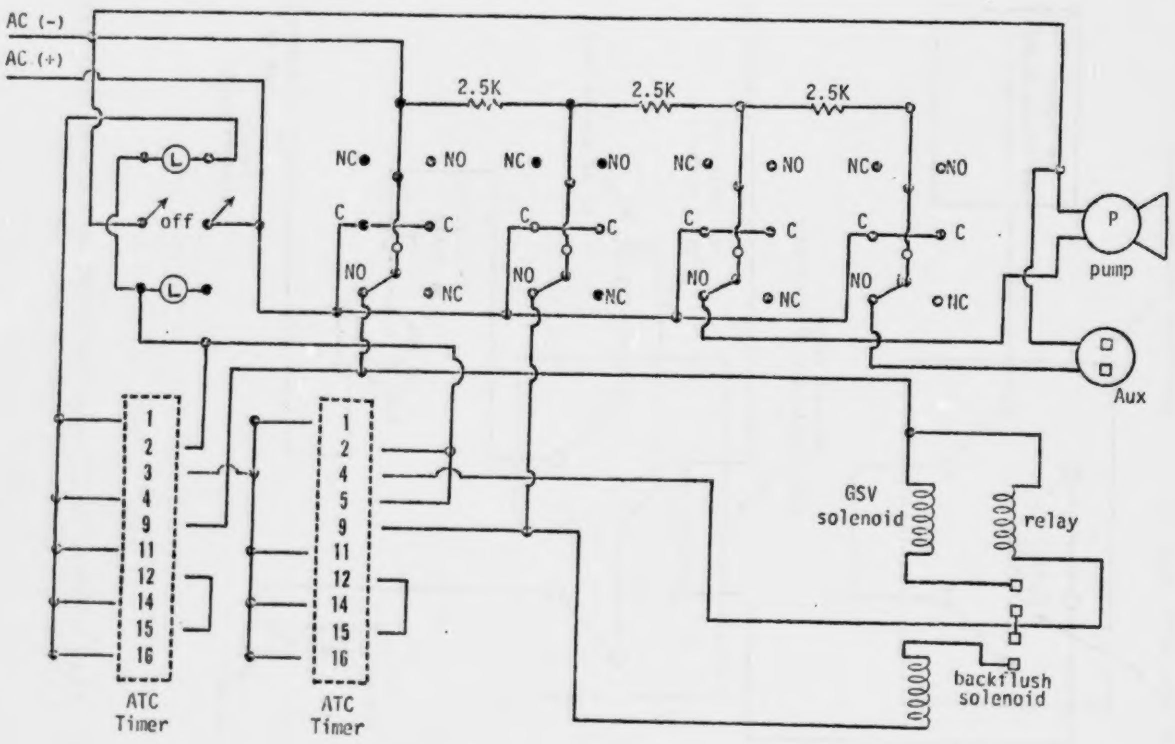

AC (-)
AC (+)
2.5K
2.5K
2.5K
NC
NO
C
off
L
ATC Timer
1
2
3
4
9
11
12
14
15
16
ATC Timer
1
2
4
5
9
11
12
14
15
16
P
pump
Aux
GSV solenoid
relay
backflush solenoid

Figure 1. Electrical schematic for organic sulfide analysis system.

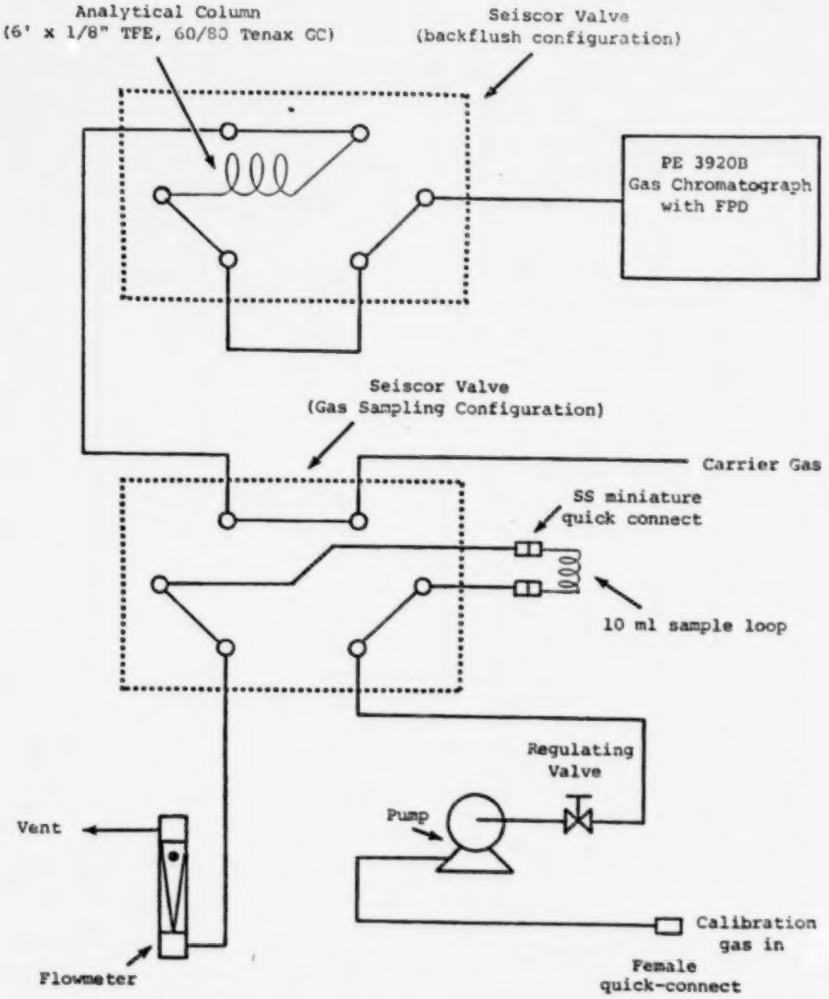

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax GC)
Seiscor Valve
(backflush configuration)
PE 3920B
Gas Chromatograph
with FPD
Seiscor Valve
(Gas Sampling Configuration)
Carrier Gas
SS miniature
quick connect
10 ml sample loop
Regulating
Valve
Pump
Vent
Flowmeter
Calibration
gas in
Female
quick-connect

Figure 2. Flow schematic of organic sulfide calibration system (Step 1 - purge of sample loop of GSV).

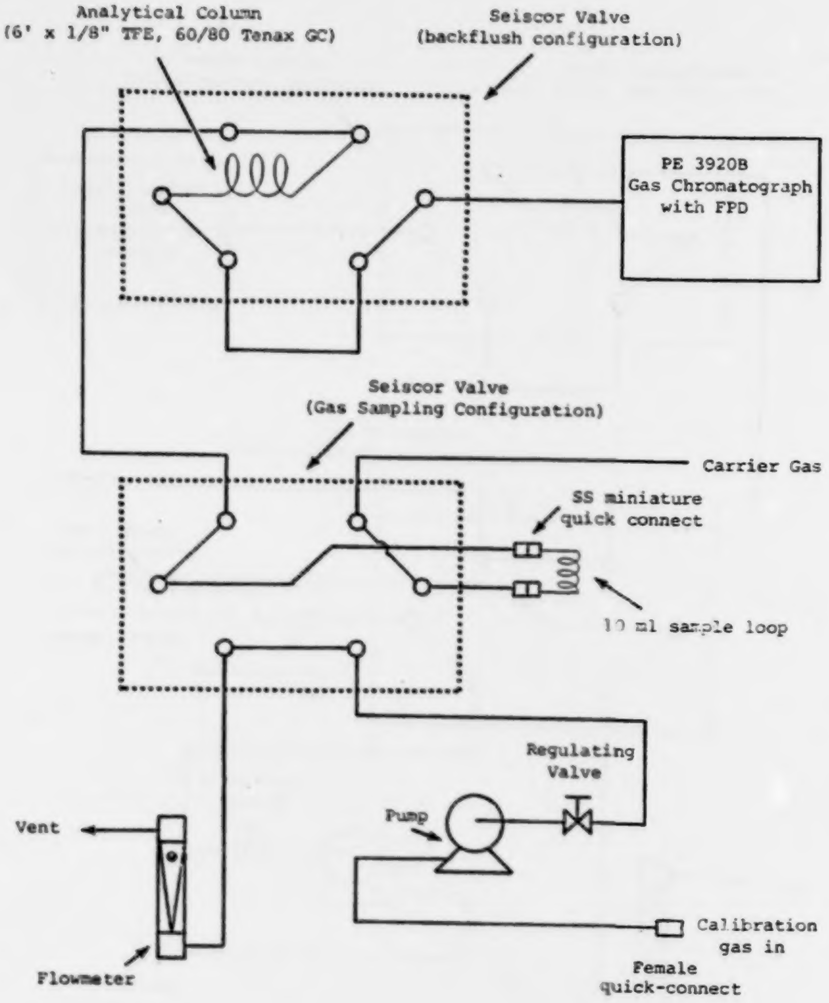

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax GC)
Seiscor Valve
(backflush configuration)
PE 3920B
Gas Chromatograph
with FPD
Seiscor Valve
(Gas Sampling Configuration)
Carrier Gas
SS miniature
quick connect
10 ml sample loop
Regulating
Valve
Pump
Vent
Flowmeter
Calibration
gas in
Female
quick-connect

Figure 3. Flow schematic of organic sulfide calibration system (Step 2 - inject calibration gas into GC system).

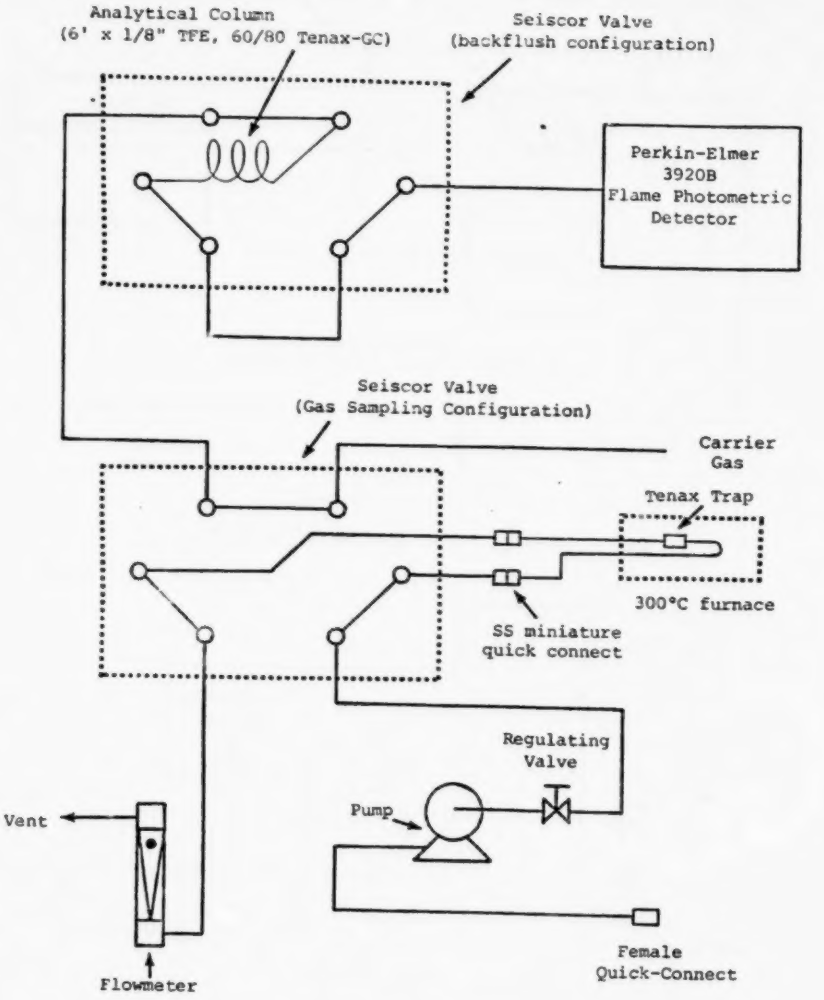

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax-GC)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920B
Flame Photometric
Detector
Seiscor Valve
(Gas Sampling Configuration)
Carrier
Gas
Tenax Trap
300°C furnace
SS miniature
quick connect
Regulating
Valve
Pump
Vent
Flowmeter
Female
Quick-Connect

Figure 4. Flow schematic of organic sulfide analysis system (Step 1 - connect Tenax trap in GSV).

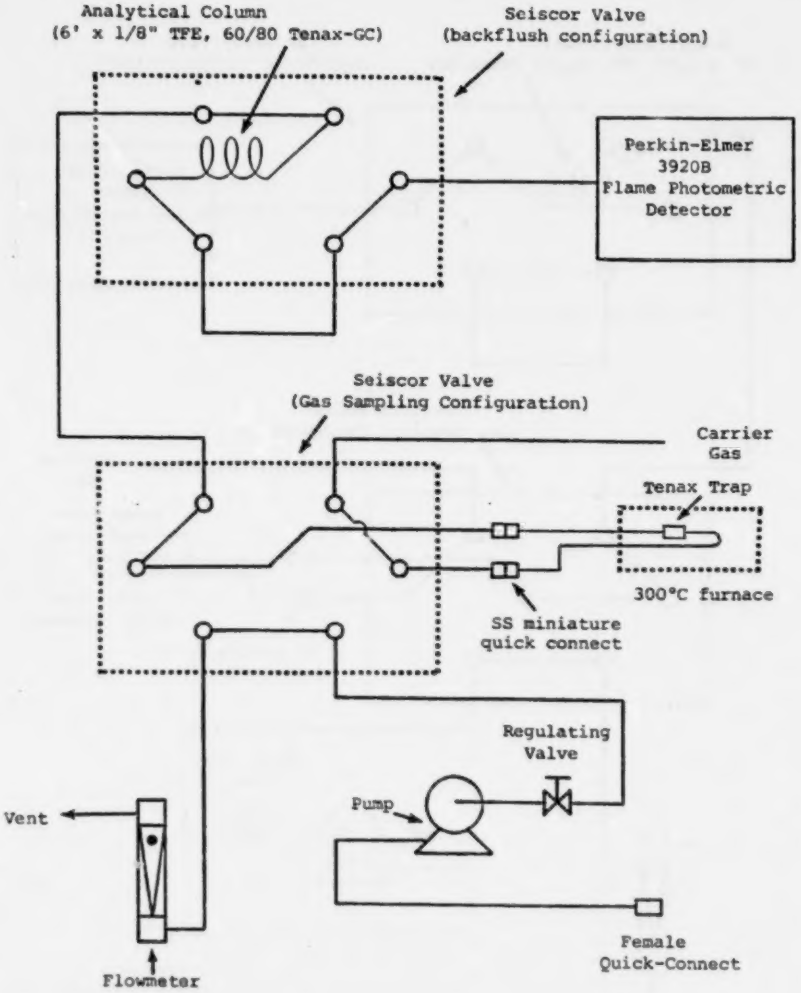

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax-GC)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920B
Flame Photometric
Detector
Seiscor Valve
(Gas Sampling Configuration)
Carrier
Gas
Tenax Trap
300°C furnace
SS miniature
quick connect
Regulating
Valve
Pump
Vent
Flowmeter
Female
Quick-Connect

Figure 5. Flow schematic of organic sulfide analysis system (Step 2 - inject Tenax trap contents into GC system).

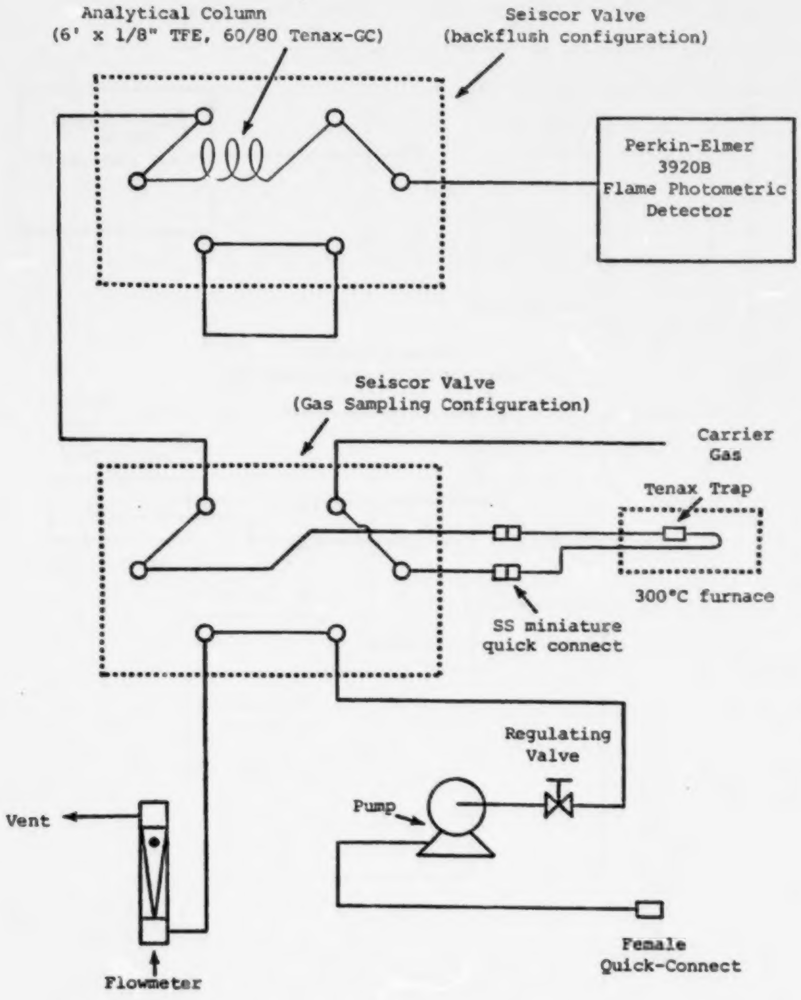

Analytical Column
(6' x 1/8" TFE, 60/80 Tenax-GC)
Seiscor Valve
(backflush configuration)
Perkin-Elmer
3920B
Flame Photometric
Detector
Seiscor Valve
(Gas Sampling Configuration)
Carrier
Gas
Tenax Trap
300°C furnace
SS miniature
quick connect
Regulating
Valve
Vent
Pump
Female
Quick-Connect
Flowmeter

Figure 6. Flow schematic of organic sulfide analysis system (Step 3 - backflush analytical column).

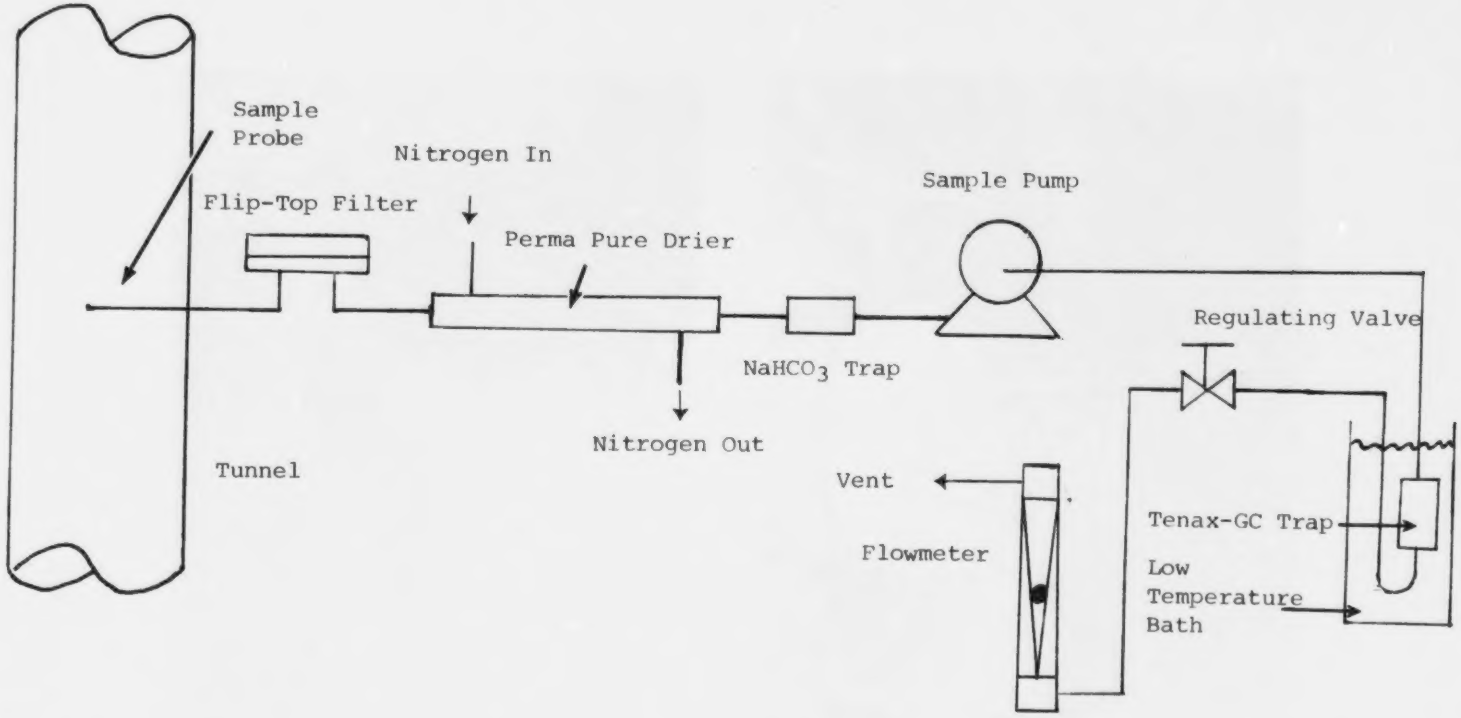

Sample
Probe
Nitrogen In
Flip-Top Filter
Perma Pure Drier
Sample Pump
Regulating Valve
NaHCO3 Trap
Nitrogen Out
Tunnel
Vent
Flowmeter
Tenax-GC Trap
Low
Temperature
Bath

Figure 7. Organic sulfide sample flow schematic.

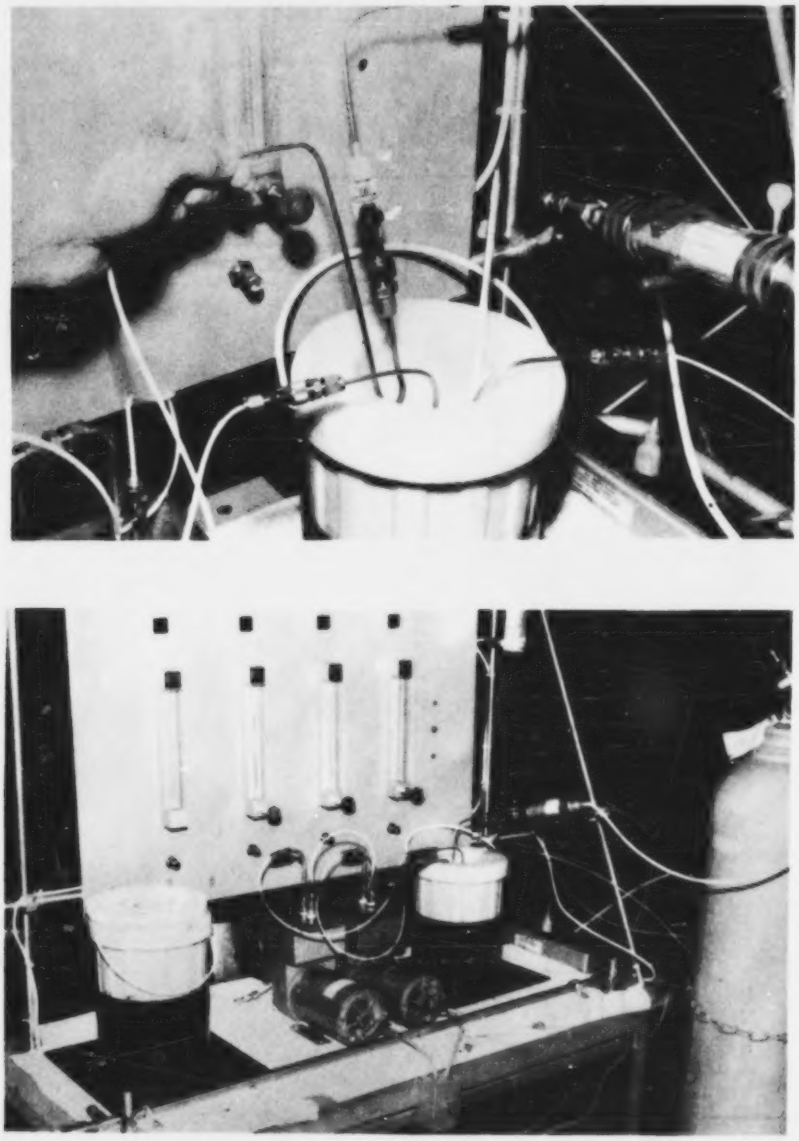


Figure 8. Several views of the organic sulfide sampling system.

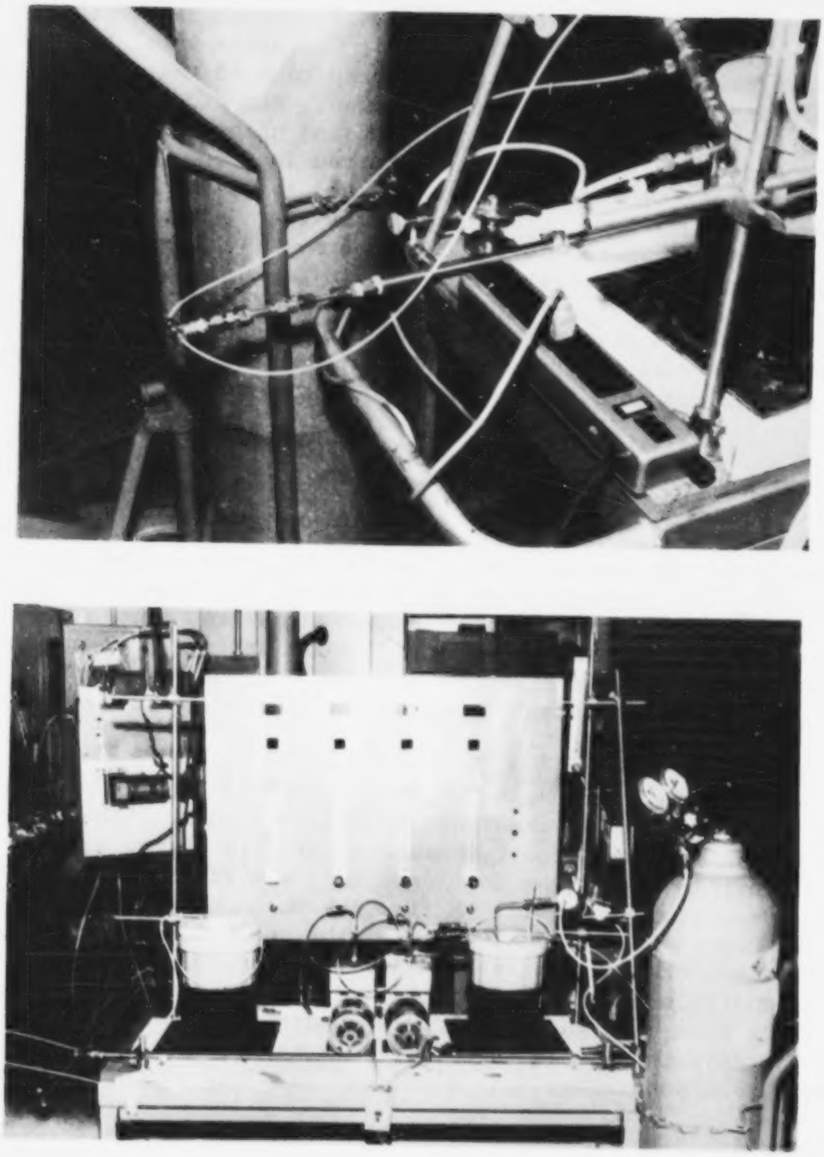


Figure 8 (Cont'd). Several views of the organic sulfide sampling system.

(sapphire float) is used to determine the exhaust sampling rate.

TRAP PREPARATION

The Tenax traps used for the collection of the organic sulfides are prepared by filling a 2" × 3/8" OD (0.028" wall) stainless steel tube with approximately 1 gram of 60/80 mesh Tenax-GC. Stainless steel fritted discs, 50μ, 3/8" OD are placed at each end of the trap to hold the Tenax in the trap while allowing a gas flow through the trap. Nut and ferrules, 3/8", and Swagelok 3/8" × 1/8" stainless steel reducing unions hold the fritted discs in place and allow the trap to be inserted into the sampling system. A 1/8" stainless steel cap is placed on each end to prevent moisture and other unwanted compounds from collecting in the trap. Figure 9 shows a view of the completed trap and of its components. When a trap is ready to use 1/8" Swagelok nuts and ferrules are used to connect 1/8" stainless steel tubing to each end of the trap. At the other end of each piece of the 1/8" stainless steel tubing a miniature male quick connect is added with 1/8" Swagelok nuts and ferrules (Figure 10). The trap can now be connected by the miniature quick connects to the sampling system or the desorbing system with ease.

ORGANIC SULFIDE TENAX-GC TRAP CONDITIONG PROCEDURE

The analysis of organic sulfides in dilute automotive exhaust requires Tenax-GC traps that have been properly conditioned. It is absolutely essential that each Tenax-GC trap undergo the identical conditioning. This will insure that there are no residual compounds in the trap from a previous sample, or in the case of a fresh trap, to remove any residual solvents. Accurate quantitative data is directly dependent on performing the conditioning procedure in a consistent manner according to the procedure outlined in section.

The Tenax-GC traps can be used repeatedly provided they are properly conditioned. Conditioning of the Tenax-GC traps is accomplished by purging with zero nitrogen at a selected temperature for a specified time period at a given flow rate. A system was developed that was capable of conditioning two Tenax-GC traps simultaneously. A flow schematic of this system is illustrated in Figure 11. Several views of the Tenax-GC sample conditioning system are presented in Figure 12. This system has been shown to reproducibly condition Tenax-GC traps to a negligible level of organic sulfides. Traps have been successfulyy re-conditioned for as many as five samples before replacing the Tenax-GC. It may be possible that the Tenax-GC traps would last substantially longer, but this has not yet been established.

The organic sulfide trap conditioning procedure is listed below in a step-wise sequence.

1.) Turn on the furnace and adjust the temperature to 325°C +25°C. The furnace should be allowed to stabilize for at least 15 minutes before the first trap is conditioned.

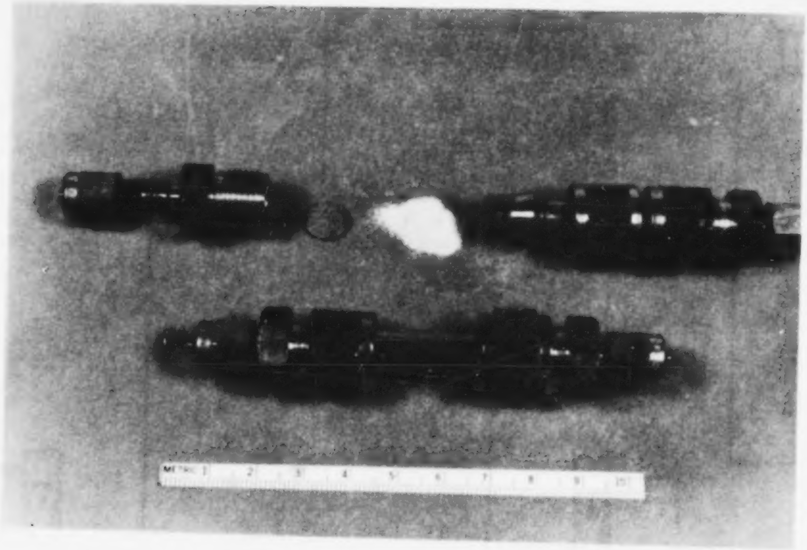

METRIC 1 2 3 4 5 6 7 8 9 10

Figure 9. Tenax-GC trap.

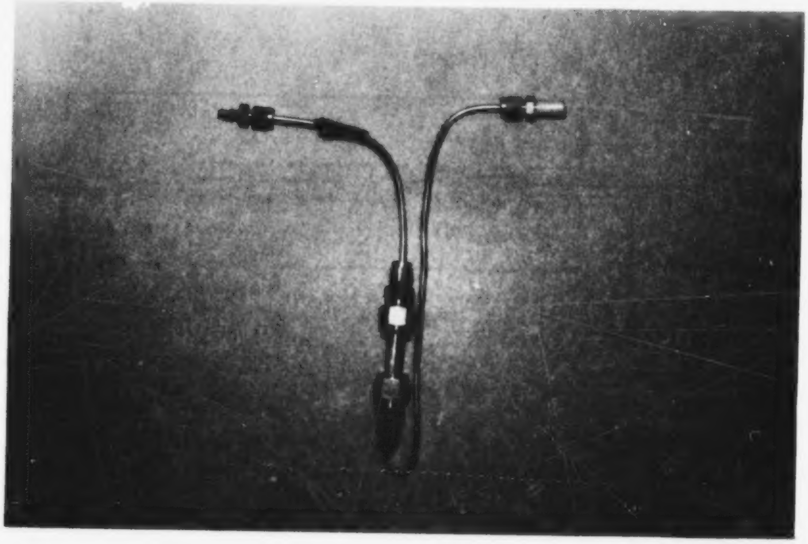


Figure 10. Tenax-GC trap with quick connect.

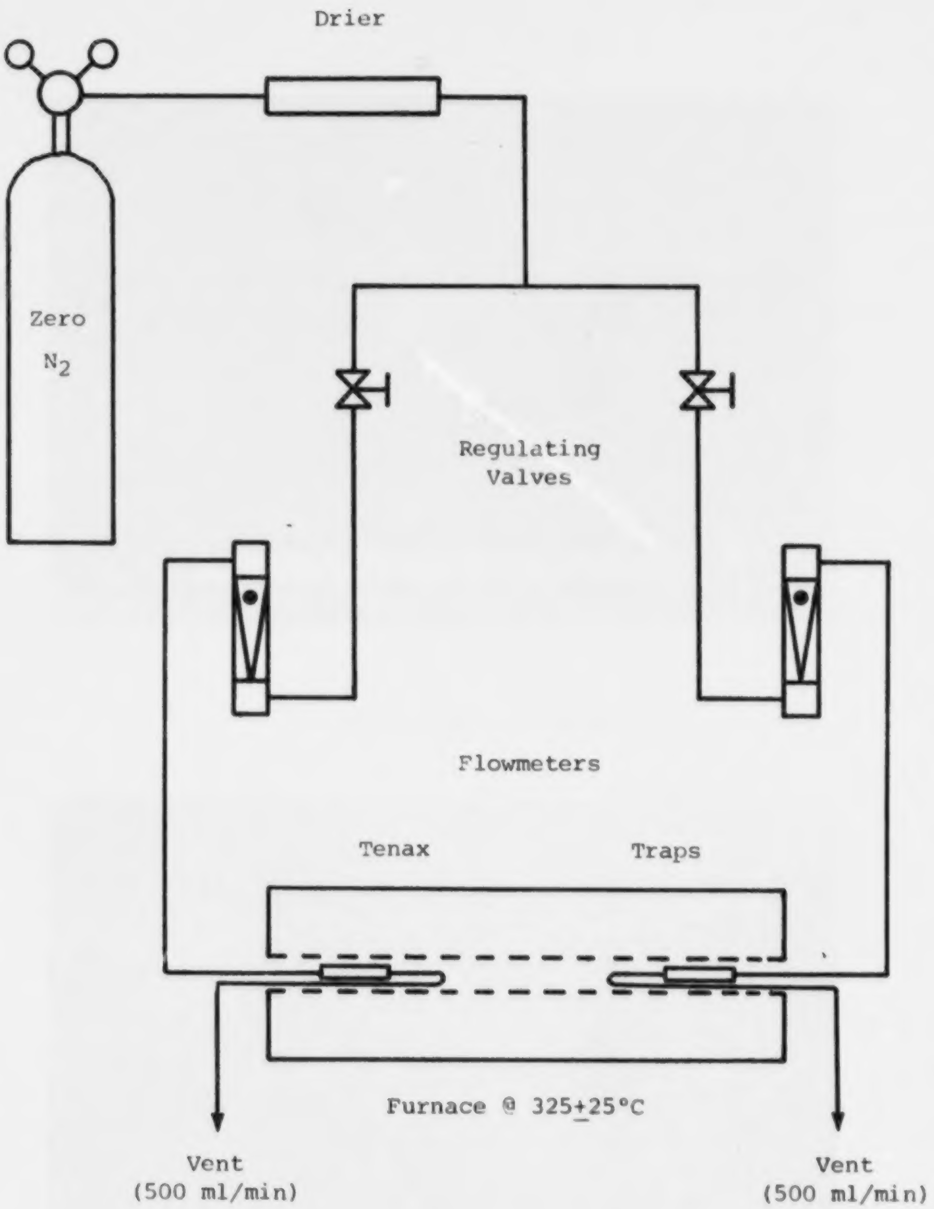

Drier
Zero
N_2
Regulating
Valves
Flowmeters
Tenax
Traps
Furnace @ 325±25°C
Vent
(500 ml/min)
Vent
(500 ml/min)

Figure 11. Flow schematic for conditioning Tenax-GC traps for organic sulfide analysis (dual system).

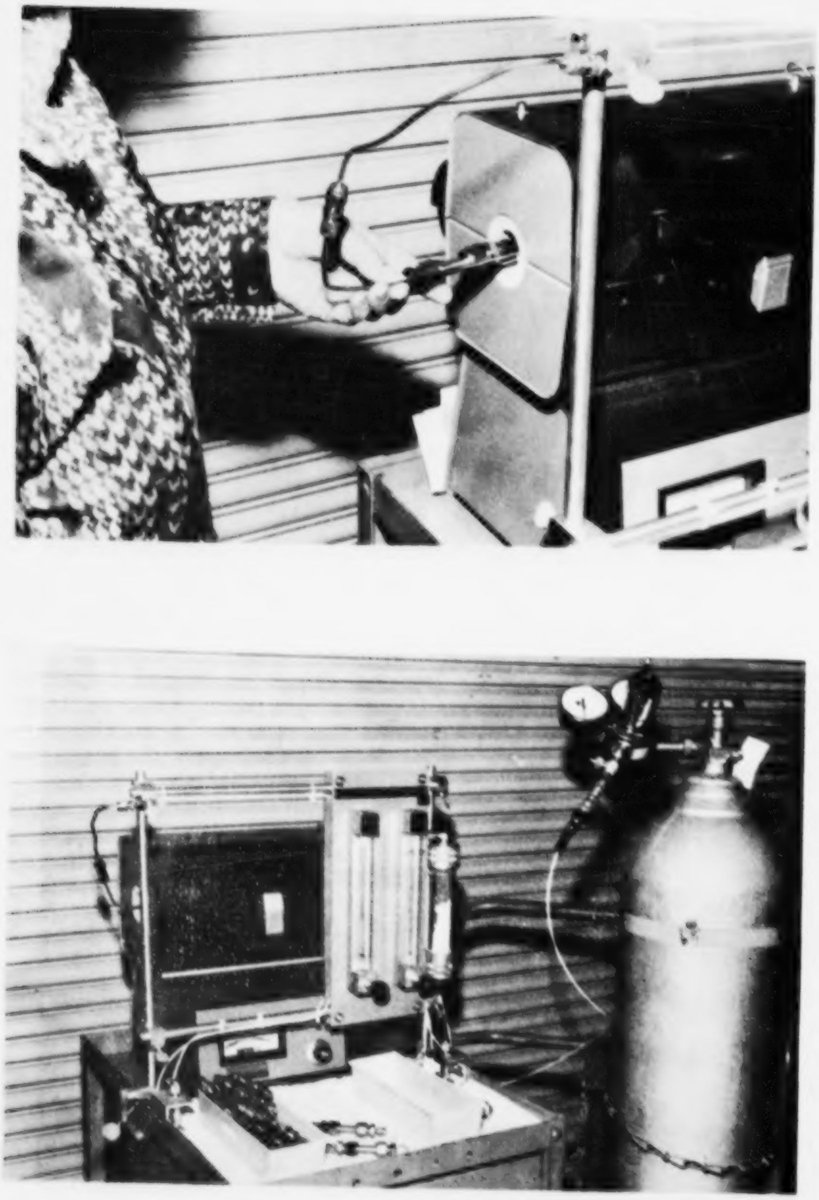
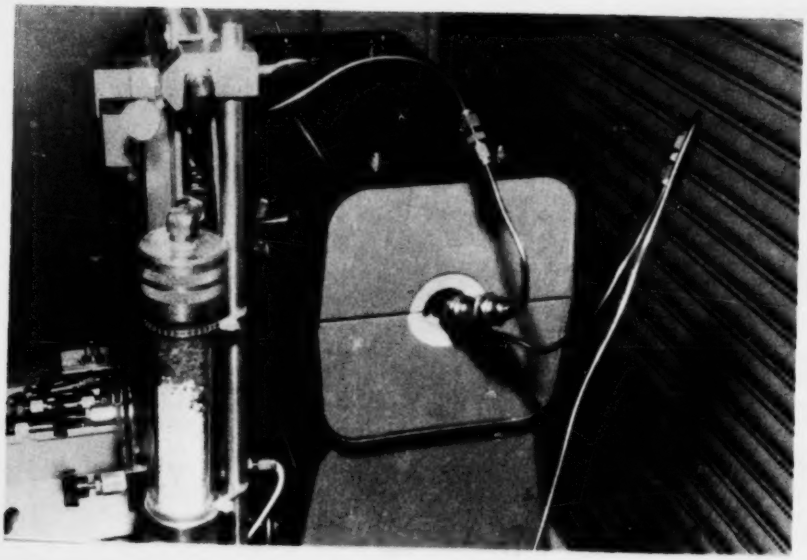


Figure 12. Several views of Tenax-GC trap conditioning system.



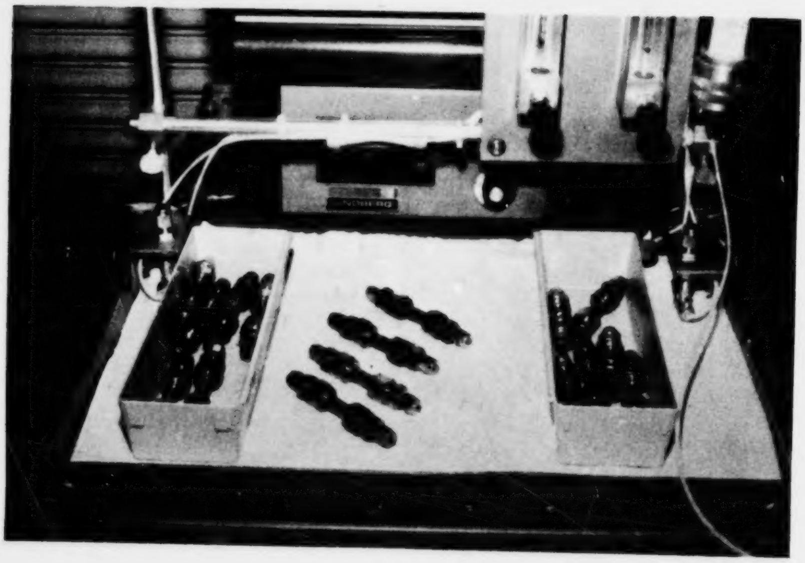


Figure 12 (Cont'd). Several views of Tenax-GC trap conditioning system.

The temperature readout on the furnace should be vertified at least once a week with a digital thermocouple.

2.) Connect the traps according to the flow schematic. Insert the traps in the furnace (with no nitrogen) and allow the traps to equilibriate for 5 minutes.

3.) Turn on the nitrogen and adjust the flow to 500 mℓ/min.

4.) After the 60 minute conditioning period, the trap is removed from the furnace and is allowed to cool to room temperature with nitrogen flowing through the trap.

5.) After the trap returns to room temperature, turn off the nitrogen and remove the trap. The system is then ready for conditioning the next two traps.

NOTE 1: A master log should be maintained on the conditioning of each trap. It is the responsibility of the individual who is conditioning the traps to keep a record of all traps that have been conditioned, who conditioned them and the date that they were conditioned. All traps should be permanently identified to enable keeping of these records.

NOTE 2: Tenax-GC traps should not be placed in the furnace if the temperature is in excess of 375°C. This is the manufacturer's maximum recommended temperature and should not be exceeded. If this is allowed to happen, the chemical and physical properties of the Tenax-GC may be altered thereby affecting the trapping characteristics of the Tenax-GC.

ANALYTICAL PROCEDURE

The analysis of the organic sulfides (carbonyl sulfide, methyl sulfide, ethyl sulfide, and methyl disulfide) in dilute exhaust is accomplished by collecting the organic sulfides in Tenax traps at -76°C. The organic sulfides are thermally desorbed from the trap into a gas chromatograph sampling system. The organic sulfides are analyzed by injecting the desorbed sample into a gas chromatograph equipped with a flame photometric detector. A standard blend containing known amounts of the four organic sulfides is injected into the gas chromatograph to quantify the results. From the GC analysis of the sample, the analysis of the standard blend, and the measured volume of exhaust sampled, the concentration of the organic sulfides in the exhaust can be determined. The analysis flow schematic for the organic sulfides is shown in Figure 13. A detailed description of the procedure follows.

The organic sulfides are removed from the exhaust stream by trapping them in Tenax GC traps. A sample pump pulls dilute exhaust from CVS through a flip top filter, to remove particulate from the exhaust sample, and then through a Perma Pure Drier which selectively removes moisture from the exhaust sample. The moisture must be removed to prevent ice from

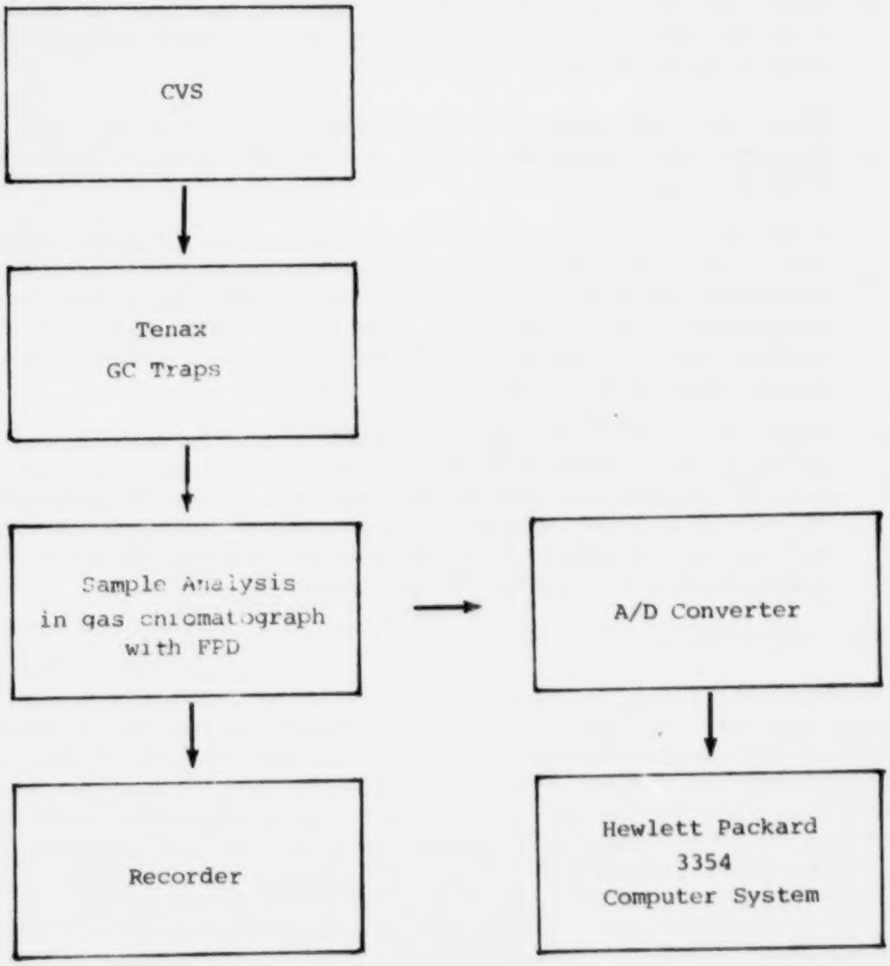

CVS
Tenax
GC Traps
Sample Analysis
in gas chromatograph
with FPD
A/D Converter
Recorder
Hewlett Packard
3354
Computer System

Figure 13. Organic sulfide analysis flow schematic.

forming in the Tenax traps. The ice formation would plug the trap and prevent the exhaust sample from passing through the trap. After exiting the Perma Pure Drier the exhaust sample passes through a sodium bicarbonate trap which removes any interfering H_2S or SO_2 in the exhaust sample. The exhaust sample is then pulled through the Tenax GC trap which removes the organic sulfides from the exhaust. The trap is held at -76°C with a dry ice-isopropyl alcohol slurry. After the organic sulfides have been removed by the Tenax trap the exhaust passes through the sample pump, a regulating valve and a flow meter before exiting the sample system. The needle valve regulates the flow through the system which is monitored by the flow meter. A constant flow of 130 mℓ/min is maintained throughout the test. The Tenax trap is disconnected from the sampling system at the two miniature quick-connects and the two male miniature quick-connects are capped. The trap remains in the -76°C dry ice-isopropyl slurry until it is desorbed by the gas chromatograph injection system.

The Tenax trap is removed from the dry ice-isopropyl slurry, the liquid is quickly wiped from the trap, and the caps are removed from the ends of the trap. The trap is connected into the gas injection system with the two quick connects, (Figure 4) and the sample is immediately injected and placed into the Lindberg furnace operating at 300°C (Figure 5). The carrier gas upon injection flows through the loop carrying the contents into the gas chromatograph where the sulfides are separated and identified by their retention times.

The gas chromatograph system used to analyze the organic sulfide sample is shown in Figure 14. The system consists of a Perkin Elmer 3920B GC, an A/D converter and a recorder. The Figure also shows the control system, the Lindberg furnace, and the Bendix valve oven. The GC is equipped with a linearized flame phtometric detector which has a high sensitivity to sulfur containing compounds. The column consists of 6' × 1/8" Teflon tubing packed with 60/80 mesh Tenax GC. The carrier gas is helium which flows through the column at 30 mℓ/min. The optimum hydrogen and air flows are 40 mℓ/min and 360 mℓ/min respectively. The column temperature, after injection of the sample, is programmed from 30°C to 140°C at 8° a minute. In a chromatogram of a standard sample (Figure 15) containing the four sulfides, the first peak eluted is carbonyl sulfide, followed by methyl sulfide, ethyl sulfide and methyl disulfide. The GC sulfide peaks are recorded on a Soltec dual channel recorder (1 mv) and peak areas and retention times are obtained from the Hewlett Packard GC computer system. A Metronix Dynacalibrator operating at 40°C and containing permeation tubes of carbonyl sulfide, methyl sulfide, ethyl sulfide, and methyl disulfide is used to supply standard concentrations of the organic sulfides. The permeation rate of each tube is monitored by monthly weighings. Zero nitrogen is used to dilute the permeation gases to the concentrations desired. The 10 mℓ sample loop is purged with this permeation gas for 10 minutes (Figure 2) and the 10 mℓ of permeation gas is then injected into the GC and analyzed. From the standard peak areas, the exhaust sample peak areas and the volume of exhaust sampled, the concentration of the organic sulfides in exhaust can be determined.

CALCULATIONS

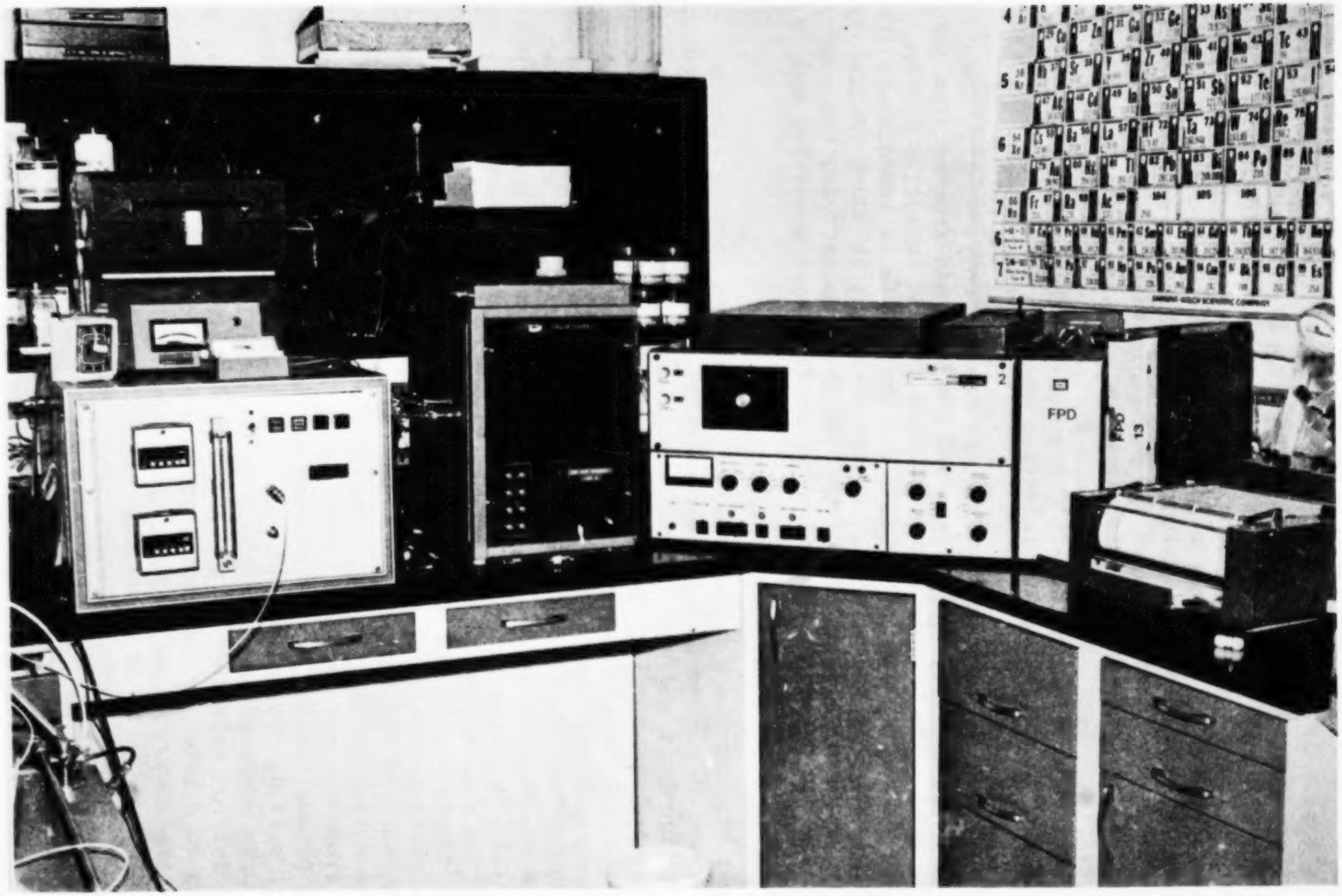
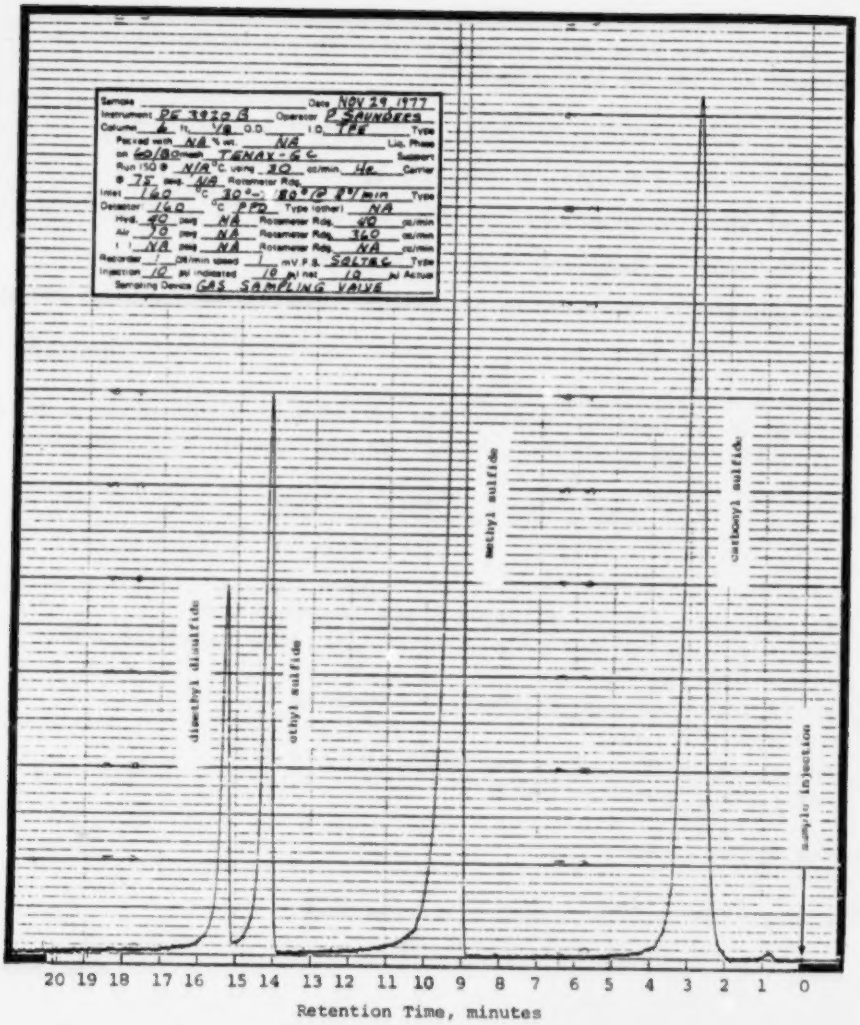


Figure 14. Organic sulfide analytical system.



Sample ________ Date NOV 29 1977
Instrument PE 3920 B Operator P. SAUNDERS
Column 6 ft. 1/8 O.D. ______ I.D. TFE Type
Packed with NA % wt. NA Liq. Phase
on 60/80 mesh TENAX-GC Support
Run ISO @ N/A °C using 30 cc/min He Carrier
@ 75 psig NA Rotameter Rdg.
Inlet 160 °C 30°→180° @ 8°/min Type
Detector 160 °C FPD Type (other) NA
Hyd. 40 psig NA Rotameter Rdg. 40 cc/min
Air 70 psig NA Rotameter Rdg. 360 cc/min
( ) NA psig NA Rotameter Rdg. NA cc/min
Recorder 1 cm/min speed 1 mV F.S. SOLTEC Type
Injection 10 µl indicated 10 µl net 10 µl Actual
Sampling Device GAS SAMPLING VALVE

dimethyl disulfide
ethyl sulfide
methyl sulfide
carbonyl sulfide
sample injection
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
Retention Time, minutes

Figure 15. Chromatogram of organic sulfide standard.

This procedure has been developed to provide the user with the concentrations of the organix sulfides (carbonyl sulfide, methyl sulfide, ethyl sulfide, and methyl disulfide) in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm for each of the sulfides. The equations for determing the concentrations of $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to find the volume of exhaust sampled from the flow rate and the sampling time by the equation:

$$\text{Vol exp (m}\ell\text{)} = \text{F.R.}_I \text{ (m}\ell\text{/min)} \times \text{Ti (sec)/60 sec/min}$$

Vol exp (mℓ) = volume of gas sample in mℓ

F.R.$_I$ (mℓ/min) = flow rate of exhaust sample in mℓ/min

Ti (sec) = sampling time in minutes

60 sec/min = conversion of sample time in seconds to minutes

[Equation 1]

The next step is to correct the volume of exhaust sampled to a standard temperature, 68°F, and pressure, 29.92" Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sample in mℓ

V_{corr} = volume of gas sample in mℓ corrected to 68°F and 29.92" Hg

P_{exp} = experimental barometric pressure

P_{corr} = 29.92" Hg

T_{exp} = experimental temperature in °F + 460

T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\text{ ("Hg)} \times V_{exp}\text{ (ft}^3\text{)} \times 528°\text{R}}{T_{exp}\text{ (°R)} \times 29.92\text{" Hg}}$$

[Equation 2]

Substituting Vol exp (mℓ) from equation 1 into equation 2 gives:

$$V_{corr}\text{ (m}\ell\text{)} = \frac{P_{exp}\text{ ("Hg)} \times \text{F.R.}_I\text{ (m}\ell\text{/min)} \times \text{Ti (sec)} \times 528°\text{R}}{T_{exp}\text{ (°R)} \times 29.92\text{" Hg} \times 60\text{ sec/min}}$$

The next step converts the volume from mℓ to cubic meters by use of the conversion factor 1 cubic meter = 10^6 mℓ.

$$V_{corr}\ (m^3) = \frac{P_{exp}\ ("Hg) \times F.R._{I}\ (m\ell/min) \times Ti\ (sec) \times 528°R}{T_{exp}\ (°R) \times 29.92"\ Hg \times 60\ sec/min \times 10^6\ m\ell/m^3}$$

[Equation 3]

The next step is to find the μg of each of the sulfides in the Tenax trap. Since the FPD has a linear response in the region of concern, then the following equation holds:

$$\frac{\mu g\ sam}{Asam} = \frac{\mu g\ std}{Astd}$$

μg sam = μg sample in Tenax trap
Asam = GC peak area of sample in relative units
μg std = μg standard
Astd = GC peak area of standard in relative units

Solving for μg sample gives:

$$\mu g\ sam = \frac{\mu g\ std \times Asam}{Astd}$$

[Equation 4]

The μg of standard for each of the organic sulfides is determined from the permeation rates of the permeation tubes containing each of the sulfides, the flow rate of the diluting gas, and the volume of gas sampled (10 mℓ).

$$\mu g\ std = \frac{P.R.\ (ng/min) \times 10\ m\ell}{F.R._{II}\ (m\ell/min) \times 1000\ ng/\mu g}$$

[Equation 5]

P.R. (ng/min) = permeation rate of permeation tube at 40° in ng/min
10 mℓ = volume of calibration gas injected
$F.R._{II}$ (mℓ/min) = flow rate of diluting gas for permeation system
1000 ng/μg = converts ng to μg, one μg equals 1000 ng

Substituting μg std from Equation 5 into Equation 4 gives:

$$\mu g\ sam = \frac{P.R.\ (ng/min) \times 10\ m\ell \times Asam}{F.R._{II}\ (m\ell/min) \times 1000\ ng/\mu g \times Astd}$$

[Equation 6]

To obtain µg sample/m^3, Equation 6 is divided by Equation 3 to give:

$$\mu\text{g sam}/_{\text{m}}3 = \frac{\text{P.R. (ng/min)} \times 10\ \text{m}\ell \times \text{Asam} \times {}^{\text{T}}\text{exp (°R)}}{\text{F.R.}_{\text{II}}\ (\text{m}\ell/\text{min}) \times 1000\ \text{ng}/\mu\text{g} \times \text{Astd} \times {}^{\text{P}}\text{exp ("Hg)}}$$

$$\times \frac{29.92\text{" Hg} \times 60\ \text{sec/min} \times 10^6\ \text{m}\ell/\text{m}^3}{\text{F.R.}_{\text{I}}\ (\text{m}\ell/\text{min}) \times \text{Ti (sec)} \times 528°\text{R}}$$

[Equation 7]

To find the concentration of each sulfide in ppm, the densities of the sulfides are needed. At 29.92" Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation

$$\frac{V}{T} = \frac{V_1}{T_1}$$

$V_1 = 22.4$

$T_1 = 32°\text{F} + 460 = 492°\text{R}$

V = volume at 68°F

$T = 68°\text{F} + 460 = 528°\text{R}$

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04 at 68°F, the density can be found in g/ℓ by dividing the molecular weight in g/mole by 24.04 ℓ/mole

$$\text{den (g/}\ell) = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}}$$

The denisty in µg/mℓ can be found by converting g to µg and ℓ to mℓ as follows:

$$\text{den}\ \mu\text{g/m}\ell = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}} \times \frac{1 \times 10^6 \mu\text{g/g}}{1 \times 10^3 \text{m}\ell/\ell} = \frac{\text{mol. wt.} \times 1000}{24.04}$$

[Equation 8]

To obtain the concentration of each sulfide in ppm, the concentration in µg/m^3 is divided by the density in µg/mℓ

$$\text{ppm} = \mu\text{g/m}^3 \div \mu\ \text{g/m}\ell = \frac{\text{m}\ell}{\text{m}^3}$$

Using Equations 7 and 8 gives the ppm concentrations in the form of the raw data.

$$\text{ppm} = \frac{\text{P.R. (ng/m}\ell) \times 10\ \text{m}\ell \times \text{Asam} \times T_{\text{exp}}\ (^\circ\text{R}) \times 29.92\text{"Hg}}{\text{F.R.}_{\text{II}}\ (\text{m}\ell/\text{min}) \times 1000\ \text{ng}/\mu\text{g} \times \text{Astd} \times P_{\text{exp}}\ (\text{"Hg})}$$

$$\times \frac{60\ \text{sec/min} \times 10^6\ \text{m}\ell/\text{m}^3}{\text{F.R.}_{\text{I}}\ (\text{m}\ell/\text{min}) \times \text{Ti (sec)} \times 528^\circ\text{R}}$$

$$\times \frac{24.04\ \ell/\text{mole}}{\text{mol. wt. (g/mole)} \times 1000\ \mu\text{g-}\ell/\text{g-m}\ell}$$

[Equation 9]

At this point, the concentration can be expressed in $\mu g/m^3$ (Equation 7) and ppm (Equation 9) at 68°F and 29.92" Hg from the raw data.

Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period a Hewlett-Packard 65 program was developed to calculate the organic sulfide concentrations in $\mu g/m^3$ and ppm from the raw data. This program is presented in Figure 16.

Sample Calculation

Assume exhaust samples were collected in Tenax traps for each portion of a three bag 1975 FTP. Raw data for these tests are presented in Figure 17. Calculations were performed using the HP-65 program and manual calculations.

Manual calculations for driving cycle FTP-1

$$\mu\text{g/m}^3\ \text{COS} = \frac{\text{P.R. (ng/m}\ell) \times 10\ \text{m}\ell \times \text{Asam} \times T_{\text{exp}}\ (^\circ\text{R}) \times 29.92\text{" Hg}}{\text{F.R.}_{\text{II}}\ (\text{m}\ell/\text{min}) \times 1000\ \text{ng}/\mu\text{g} \times \text{Astd} \times P_{\text{exp}}\ (\text{"Hg})}$$

$$\times \frac{60\ \text{sec/min} \times 10^6\ \text{m}\ell/\text{m}^3}{\text{F.R.}_{\text{I}}\ (\text{m}\ell/\text{min}) \times \text{Ti (sec)} \times 528^\circ\text{R}}$$

$$= \frac{667.5\ \text{ng/m}\ell \times 10\ \text{m}\ell \times 30200 \times 535^\circ\text{R} \times 29.92\text{" Hg}}{580\ \text{m}\ell/\text{min} \times 1000\ \text{ng}/\mu\text{g} \times 18514 \times 29.80\text{" Hg}}$$

$$\times \frac{60\ \text{sec/min} \times 10^6\ \text{m}\ell/\text{m}^3}{130\ \text{m}\ell/\text{min} \times 504 \times 528^\circ\text{R}}$$

$$= 17.5\ \mu\text{g/m}^3$$

HP-65 Program Form

Title Organic Sulfides in Exhaust Page ____ of ____

SWITCH TO W/PRGM PRESS f PRGM TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23	
A	11	In Samp Flow, ml/min
3		
4		
0		
0		
0		
÷	81	
R/S	84	In Sampling Time, sec
X	71	
R/S	84	In Barometer, "Hg
X	71	
STO1	3301	
R/S	84	In Samp Temp, °F
4		
6		
0		
+	61	
RCL1	3401	
g x⇄y	3507	
÷	81	
g 1/x	3504	
R/S	84	In Dil Gas Flow, ml/min
÷	61	
STO2	3302	
R/S	84	In Perm Rate COS, ng/min
RCL2	3402	
X	71	
R/S	84	In Std Area COS
÷	81	
R/S	84	In Samp Area COS
X	71	
R/S	84	Out $\mu g/m^3$ COS
2		
4		
9		
9		
÷	81	
R/S	84	Out ppm COS
		In P R $(CH_3)_2S$, ng/min
RCL2	3402	
X	71	
R/S	84	In Std Area $(CH_3)_2S$
÷	81	
R/S	84	In Samp Area $(CH_3)_2S$
X	71	
R/S	84	Out $\mu g/m^3$ $(CH_3)_2S$
2		
5		
8		
4		
÷	81	
R/S	84	Out ppm $(CH_3)_2S_2$
		In P R $(C_2H_5)_2S$, ng/min
RCL2	3402	
X	71	
R/S	84	In Std Area $(C_2H_5)_2S$
÷	81	
R/S	84	In Samp Area $(C_2H_5)_2S$
X	71	
R/S	84	Out $\mu g/m^3$ $(C_2H_5)_2S$
3		
7		
5		
2		
÷	81	
R/S	84	Out ppm $(C_2H_5)_2S$
		In P R $(CH_3)_2S_2$, ng/min
RCL2	3402	
X	71	
R/S	84	In Std Area $(CH_3)_2S_2$
÷	81	
R/S	84	In Samp Area $(CH_3)_2S_2$
X	71	
R/S	84	Out $\mu g/m^3$ $(CH_3)_2S_2$
3		
9		
1		
8		
÷	81	
R/S	84	Out ppm $(CH_3)_2S_2$
RTN	24	

REGISTERS

R_1 ____
R_2 ____
R_3 ____
R_4 ____
R_5 ____
R_6 ____
R_7 ____
R_8 ____
R_9 ____

LABELS

A ____
B ____
C ____
D ____
E ____
0 ____
1 ____
2 ____
3 ____
4 ____
5 ____
6 ____
7 ____
8 ____
9 ____

FLAGS

1 ____
2 ____

Figure 16. HP-65 program.

HP-65 User Instructions

Title ______________________________ Page ____ of ____

Programmer ______________________________ Date ________

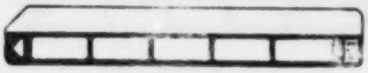
STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on; switch to run				
0_2	Feed card in from right to left				
0_3	Initialize		f	REG	
0_4	Set decimal place		DSP	2	
1	Input Sample Flow Rate, ml/min		A		
2	Input Sampling Time, sec		R/S		
3	Input Barometric Pressure, "Hg		R/S		
4	Input Sample Temperature, °F		R/S		
5	Input Dilution Gas Flow for Perm Stds, ml/min		R/S		
6	Input Permeation Rate COS, ng/min		R/S		
7	Input Standard Area COS		R/S		
8	Input Sample Area COS		R/S		
	Output Conc µg/m^3 COS		R/S		
	Output Conc ppm COS				
9	Input Permeation Rate $(CH_3)_2S$, ng/min		R/S		
10	Input Standard Area $(CH_3)_2S$		R/S		
11	Input Sample Area $(CH_3)_2S$		R/S		
	Output Conc µg/m^3 $(CH_3)_2S$		R/S		
	Output Conc ppm $(CH_3)_2S$				
12	Input Permeation Rate $(C_2H_5)_2S$, ng/min		R/S		
13	Input Standard Area $(C_2H_5)_2S$		R/S		
14	Input Sample Area $(C_2H_5)_2S$		R/S		
	Output Conc µg/m^3 $(C_2H_5)_2S$		R/S		
	Output Conc ppm $(C_2H_5)_2S$				
15	Input Permeation Rate $(CH_3)_2S_2$, ng/min		R/S		
16	Input Standard Area $(CH_3)_2S_2$				

Figure 16 (Cont'd). HP-65 program.

HP-65 User Instructions

Title ______________________________ Page ____ of ____

Programmer ______________________________ Date ________



STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
17	Input Sample Area $(CH_3)_2S_2$		R/S		
	Output Conc µg/m^3 $(CH_3)_2S_2$		R/S		
	Output Conc ppm $(CH_3)_2S_2$				
			RTN		
			f		
			REG		
			CL_x		

Figure 16 (Cont'd). HP-65 program.

SWRI PROJECT NO. ________ TEST NO. ____________ TEST DATE: __________ VEHICLE: ____________

FUEL: _________ CVS NO. _________ TUNNEL SIZE: _________ DRIVER: ________ MILES: ____________

SAMPLE COLLECTION BY: __________ CHEMICAL ANALYSIS BY: ________ CALCULATIONS BY: ___________

GENERAL COMMENTS: ____

Test No.	1	2	3	4	5	6
Driving Cycle	FTP-1	FTP-2	FTP-3	SET-7	HFET	NYCC
Sample Flow Rate, ml/min	130	110	150	90	120	170
Sampling Time, sec	504	867	505	1397	765	1200
B. P., "Hg	29.80	30.03	29.02	29.25	29.95	29.50
Temp, °F	75	80	96	85	83	89
Dilution Gas Flow, ml/min	580	500	600	650	450	575
Permeation Rate COS, ng/min	667.5	667.5	667.5	667.5	667.5	667.5
Standard Area COS	18,514	20,112	21,238	16,542	15,962	23,146
Sample Area COS	30,200	40,100	33,162	20,122	16,269	32,641
Sample Conc. COS, µg/m^3	17.5	17.1	14.9	6.29	10.2	5.08
Sample Conc COS, ppm	0.00700	0.00683	0.00598	0.00252	0.00406	0.00203
Permeation Rate $(CH_3)_2S$ ng/min	1061	1061	1061	1061	1061	1061
Standard Area $(CH_3)_2S$	41,006	38,100	35,100	41,000	45,610	35,122
Sample Area $(CH_3)_2S$	50,716	40,381	49,162	38,142	54,753	41,611
Sample Conc $(CH_3)_2S$, µg/m^3	21.1	14.4	21.3	7.65	19.0	6.78
Sample Conc $(CH_3)_2S$, ppm	0.00816	0.00558	0.00824	0.00296	0.00736	0.00262
Permeation Rate $(C_2H_5)_2S$, ng/min	445	445	445	445	445	445
Standard Area $(C_2H_5)_2S$	6971	7017	6844	6015	7113	7099
Sample Area $(C_2H_5)_2S$	31,649	34,650	32,111	7022	7914	17,416
Sample Conc $(C_2H_5)_2S$, µg/m^3	32.5	28.2	29.9	4.03	7.39	5.89
Sample Conc $(C_2H_5)_2S$, ppm	0.00865	0.00751	0.00798	0.00107	0.00197	0.00157
Permeation Rate $(CH_3)_2S_2$, ng/min	133.5	133.5	133.5	133.5	133.5	133.5
Standard Area $(CH_3)_2S_2$	2315	2210	2763	1651	1814	2917
Sample Area $(CH_3)_2S_2$	2011	3120	6372	1561	1418	2372
Sample Conc $(CH_3)_2S_2$, µg/m^3	1.86	2.42	4.41	0.978	1.56	0.586
Sample Conc $(CH_3)_2S_2$, ppm	0.000475	0.000617	0.00113	0.00250	0.000397	0.000149

Figure 17. Organic sulfide sample collection sheet.

ppm COS = $\mu g/m^3 \div$ density $\mu g/m\ell$

$$\text{density } \mu g/m = \frac{\text{mol. wt. (COS)} \times 1000}{24.04\ell}$$

mol. wt. COS = 60.08 g/mole

$$\text{density} = \frac{60.08 \text{ g/mole} \times 1000}{24.04 \ \ell/\text{mole}} = 2499 \ \mu g/m$$

$$\text{ppm} = 17.5 \ \mu g/m^3 \div 2499 \ \mu g/m\ell = 7.00 \times 10^{-3} \ m\ell/m^3 = 7.00 \times 10^{-3} \text{ ppm}$$

The calculations for methyl sulfide, ethyl sulfide, and methyl disulfide are carried out in the same manner by substituting in the appropriate permeation rates, standard areas, sample areas, and molecular weights into the above formulas. These calculation give the following concentrations: $(CH_3)_2S$, 21.1 $\mu g/m^3$ and 0.00816 ppm; $(C_2H_5)_2S$, 32.5 $\mu g/m^3$ and 0.00865 ppm; and $(CH_3)_2S_2$, 1.86 $\mu g/m^3$ and 0.000475 ppm.

NOTE: The values used in these calculations are picked from a range of temperatures, pressures, etc. to validate the calculations and may not be representative of expected raw data. These calculations are presented to confirm that manual and HP-65 calculations give the same results. This was confirmed for six sets of calculations.

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APPENDIX J

NICKEL CARBONYL PROCEDURE

THE MEASUREMENT OF NICKEL CARBONYL IN EXHAUST

The concentration of nickel carbonyl, $Ni(CO)_4$, in exhaust can be determined by the use of a chemiluminescent NO_x analyzer modified with a No. 54 wratten filter. Standard CVS bag samples are analyzed for nickel carbonyl using standard calibration blends to quantify the results. The instrument has a linear response from 0.1 ppm down to its detection limits (less than 1 ppb). The linearity at higher concentrations was not determined. The total system schematic for the analysis of nickel carbonyl is shown in Figure 1.

LIST OF EQUIPMENT

The equipment for the analysis of nickel carbonyl is divided into two parts. The first part involves the analysis of the exhaust sample and the second, the nickel carbonyl blend dilution system. Manufacturer, stock number, and any pertinent descriptive information are listed.

Analysis

1. Chemiluminescent analyzer, Thermo Electron Corporation Model 12A, modified by replacing the factory installed filter with a Kodak No. 54 Wratten filter.
2. Quartz tube furnace, Lindberg Sola Basic.
3. Quartz tubing, 5/16" OD × 42".
4. Sample pump, Thomas, Model No. 106 CA 18 3.
5. Recorder, Texas Instruments, 10 mV.
6. Modified 25 mm A-H microanalysis filter holder, Millipore, Catalog No. XX50 025 00.
7. Fluoropore 25 mm filters, Millipore, Catalog No. FHLP 025 00, 0.5 micron pore size.
8. Female quick connects, stainless steel.
9. Miscellaneous stainless steel, brass, and Teflon nuts, ferrules, unions, tees, connectors, etc.
10. Miscellaneous Teflon tubing (1/4", 5/16", and 3/8").
11. Flowmeter, Brooks Instrument Division, R-2-15-A, with glass float,

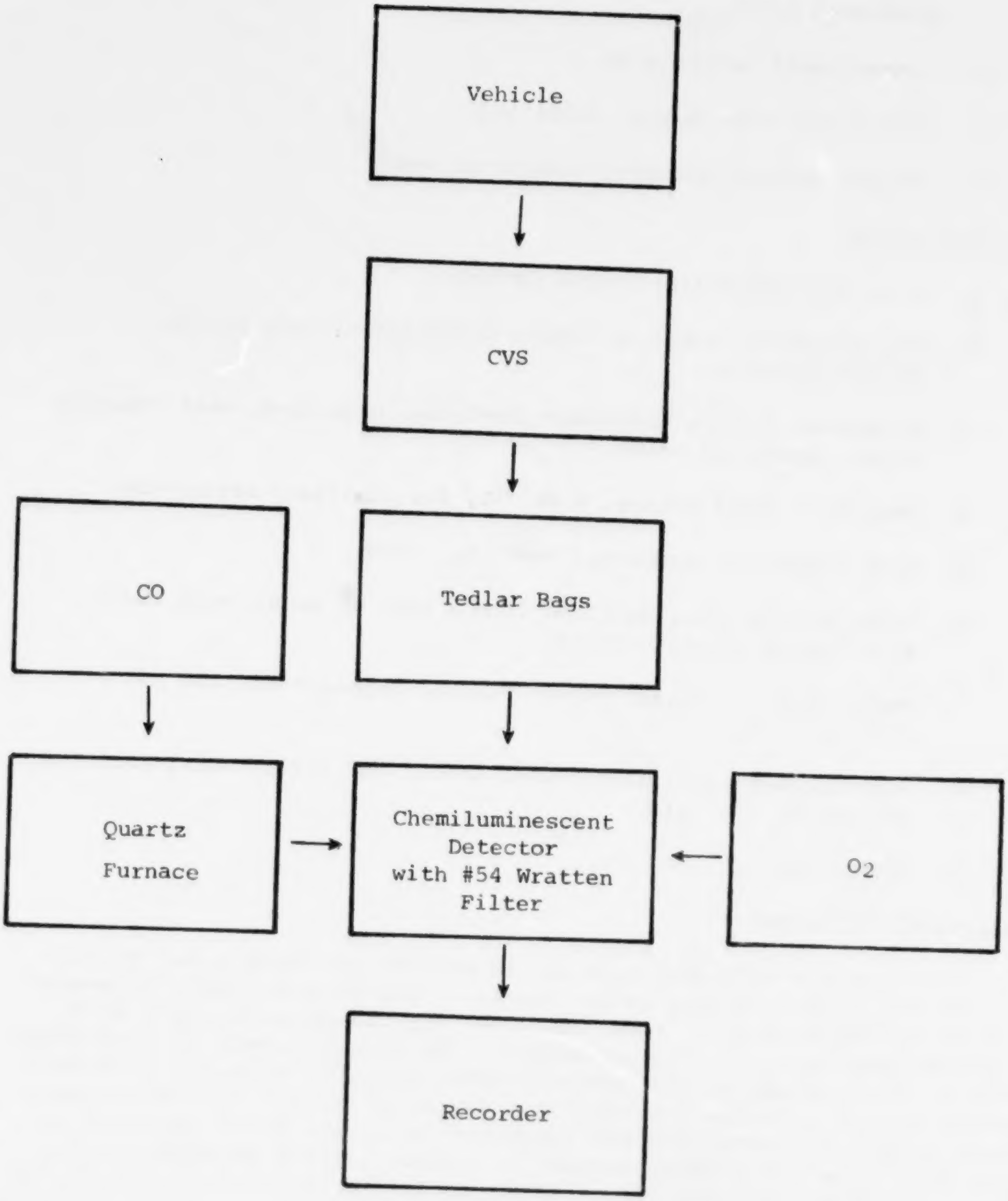
Vehicle
CVS
CO
Tedlar Bags
Quartz Furnace
Chemiluminescent Detector with #54 Wratten Filter
O_2
Recorder

Figure 1. Nickel carbonyl analysis flow schematic.

graduated 0-150°

12. Concentrated nitric acid.

13. Carbon monoxide, Airco, Grade 2.3.

14. Oxygen, Liquid Carbonic, industrial grade.

Dilution System

1. Zero compressed air, Liquid Carbonic.

2. Dry gas meter, American Singer Corporation, Type AL-120, 60 cfm capacity.

3. Flowmeter, Brooks Instrument Division, R-16-16-A, with sapphire float, graduated 0-100.

4. Stainless steel tubing, 0.01" ID, for capillary restrictor.

5. Line regulator, Matheson, Model No. 40-H.

6. Glass mixing bulb, modified from a 1000 mℓ bubble soap meter, with Teflon mixing baffles.

7. Teflon tubing, United States Plastic Corporation, 1/4" OD × 1/8" ID.

8. Miscellaneous stainless steel, brass, and Teflon nuts, ferrules, unions, valves, etc.

9. Copper tubing, 1/8" OD.

ANALYTICAL PROCEDURE

The analysis of nickel carbonyl in exhaust is accomplished by collecting the dilute exhaust in bag samples. The exhaust sample in pumped out of the bag through a filter to remove any nickel particulate which might be present in the exhaust sample. The exhaust sample is then mixed with an equal volume of ~100 percent carbon monoxide which has previously passed through a quartz furnace. The mixture of exhaust and carbon monoxide enters the chemiluminescent analyzer where the nickel carbonyl reacts with ozone and carbon monoxide to produce a light emitting species. The interfering light emitted by nitric oxide (NO) and olefins is removed by the use of a Kodak No. 54 wratten filter. The response of the detector to the emitted light is then compared with the response to a diluted standard nickel carbonyl blend. This comparison allows the concentration of nickel carbonyl in exhaust to be determined. Figure 2 shows a schematic of the analysis system along with a system for diluting nickel carbonyl blends to less than 1 ppb. A detailed description of the procedure follows.

For the analysis of nickel carbonyl, dilute exhaust is collected from

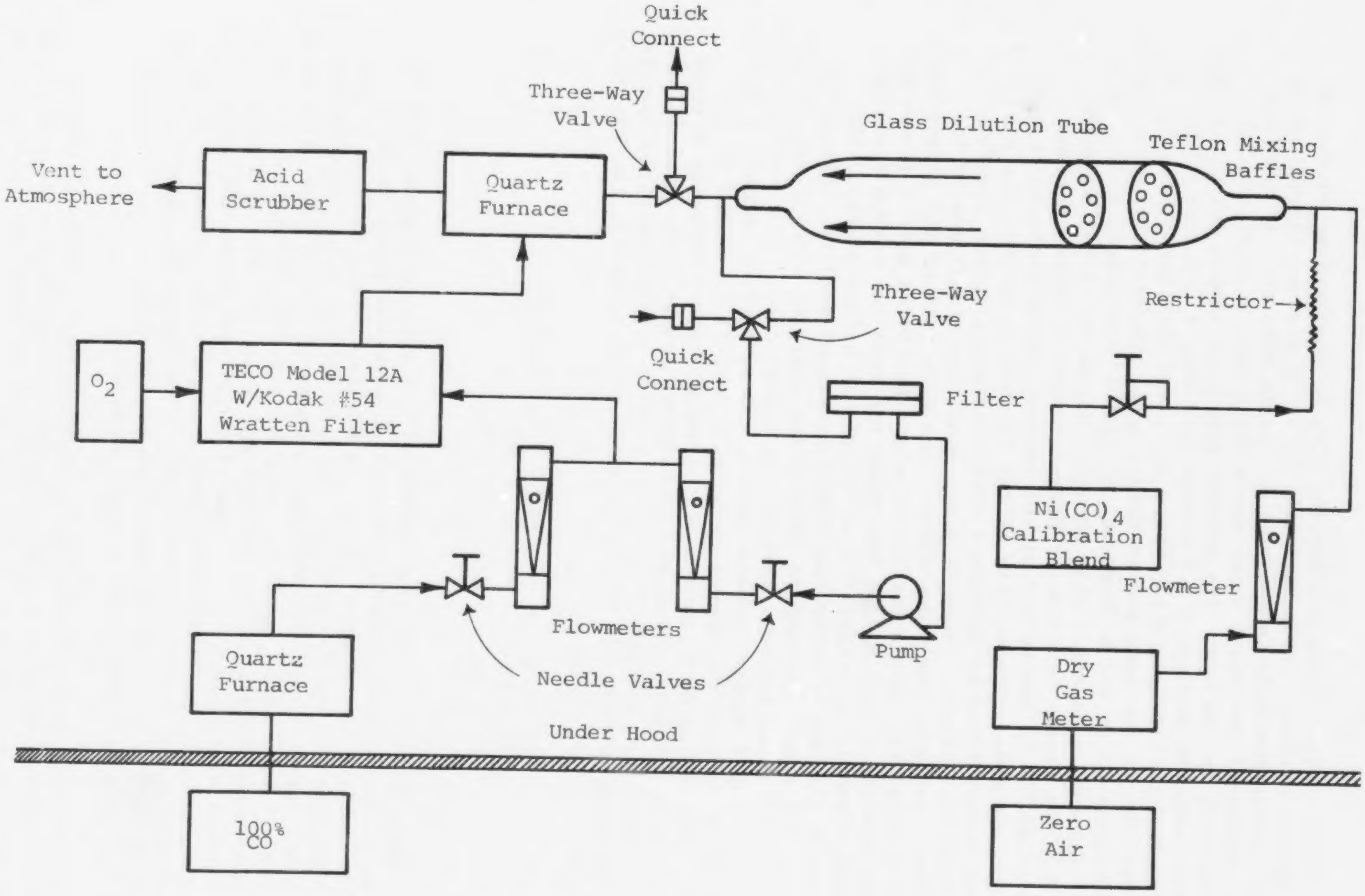
Quick
Connect
Three-Way
Valve
Glass Dilution Tube
Teflon Mixing
Baffles
Vent to
Atmosphere
Acid
Scrubber
Quartz
Furnace
Three-Way
Valve
Restrictor
Quick
Connect
Filter
O_2
TECO Model 12A
W/Kodak #54
Wratten Filter
$Ni(CO)_4$
Calibration
Blend
Flowmeter
Flowmeters
Pump
Quartz
Furnace
Needle Valves
Dry
Gas
Meter
Under Hood
100%
CO
Zero
Air

Figure 2. Nickel carbonyl analysis and dilution system flow schematic.

the CVS in Tedlar bags. These bag samples must be analyzed as quickly as possible. Nickel carbonyl has a half life of 40-70 minutes (depending on the level of carbon monoxide in the bag) in dilute exhaust. If the bags sit for any prolonged length of time, there would be a significant loss of nickel carbonyl in the bag. The exhaust sample is pumped out of the bag with a sample pump and through a 0.5 micron pore size Fluoropore filter to remove any nickel particulate which would interfere with the analysis. The sample passes through the pump and is forced under pressure through a needle valve (to regulate flow) and a flowmeter to monitor the sample flow. At this point, the sample is mixed with an equal volume of carbon monoxide. Before mixing, the carbon monoxide is passed through a quartz furnace (operating at 480°C) to remove any nickel carbonyl which might be present in the carbon monoxide. The ability of the furnace to destroy the nickel carbonyl was demonstrated by passing a nickel carbonyl-carbon monoxide sample through the furnace. When this was done, the signal due to the nickel carbonyl was completely destroyed. The flow rate of the carbon monoxide is also regulated with a needle valve and monitored with a flowmeter. Under normal operating conditions, the flows for both the carbon monoxide and the exhaust sample are regulated at 165 mℓ/min before mixing. The carbon monoxide and sample enter the chemiluminescent analyzer through the sample line. The sample mixture is split in the analyzer with 95 percent of the mixture exiting the analyzer through the bypass line. This exiting mixture passes through a quartz furnace (480°C) and is bubbled through a nitric acid scrubber to destroy the nickel carbonyl before it is vented to the atmosphere. The remaining 5 percent of the sample-carbon monoxide mixture enters the reaction chamber where nickel carbonyl reacts with ozone (generated by the analyzer) and carbon monoxide to give a light emitting species. The light emitting species has been postulated to be formed by the following series of reactions.

$$
\begin{aligned}
Ni(CO)_4 + O_3 &\rightarrow NiO + \text{other products} \\
NiO + CO &\rightarrow Ni + CO_2 \\
Ni + O_3 &\rightarrow NiO^* + O_2 \\
NiO^* &\rightarrow NiO + h\nu
\end{aligned}
$$

The higher sensitivity of the instrument (<1 ppb) is probably due to the ability of each nickel molecule to undergo numerous light emitting steps before exiting the chamber. A No. 54 wratten filter is used to prevent the light emitted by nitric oxide, NO, and olefins from entering the photomultipler tube. These compounds are present in exhaust and react with ozone to give light emitting species. Without removing the signal due to these species, the analysis of nickel carbonyl would be very difficult. An 80 ppm nitric oxide sample gives a signal two to three times the noise level of the instrument and a mixture of olefins (34 ppm total) gives no signal at all when using the No. 54 wratten filter. The instrument gives a linear response from ∿0.1 ppm nickel carbonyl down to its detection limits. The linearity at higher concentration was not determined.

The results are quantified by using diluted nickel carbonyl blends. Aluminum cylinders containing nickel carbonyl in carbon monoxide are stored outside in a metal cage (Figure 3) and the blend is piped into the building with copper tubing. The cylinders are named by wet chemistry. To dilute

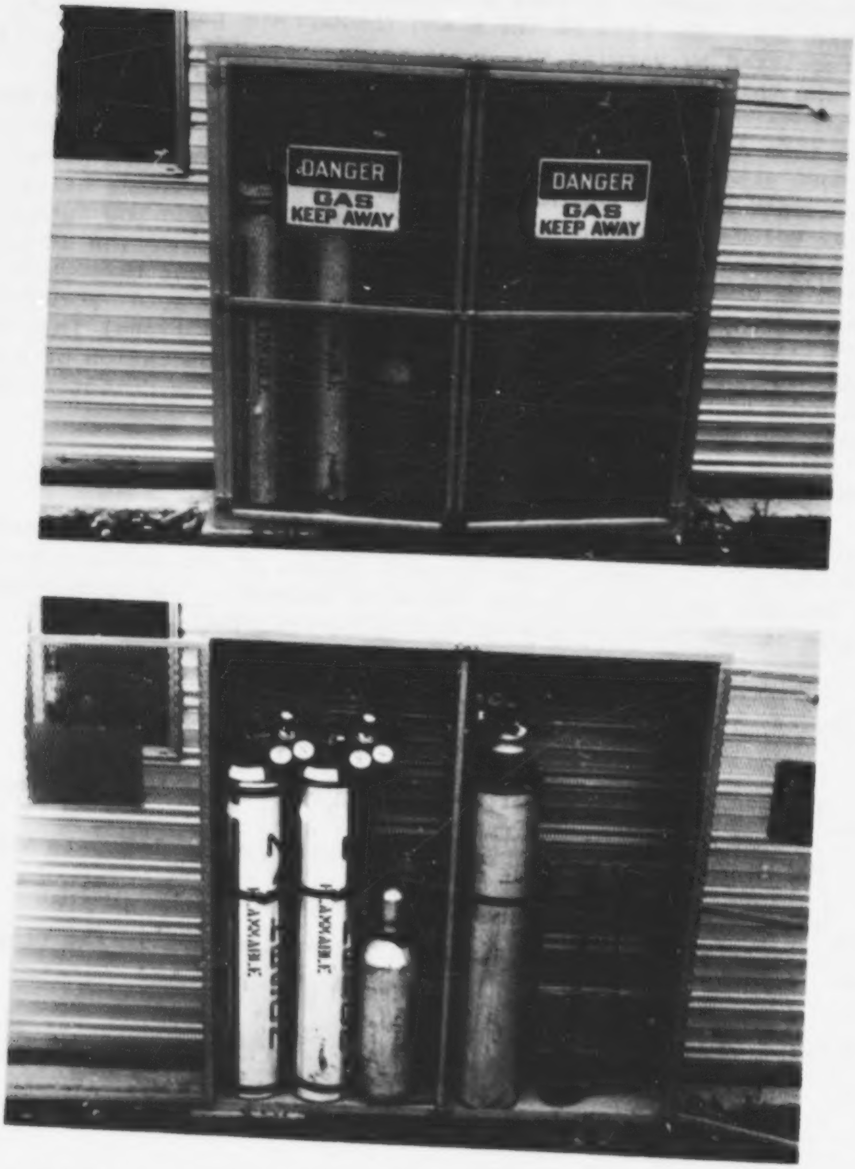
DANGER
GAS
KEEP AWAY
DANGER
GAS
KEEP AWAY

Figure 3. Storage of nickel carbonyl calibration blends.

the concentration of nickel carbonyl in the blend down to the levels of interest, the blend passes through stainless steel capillary tubing and into a glass mixing chamber (Figure 4) where it is mixed with a large volume of zero air. The flow of the blend through the capillary, 3-50 mℓ/min, is regulated by varying the pressure on the capillary with a line regulator. The volume of zero air that enters the mixing chamber, 0.5 to 8 liters a minute, is monitored with both a dry gas meter and a flowmeter. A portion of this diluted blend is pumped out of the chamber and through a 0.5 micron pore size Fluoropore filter. The diluted blend then passes through the sample pump, a needle valve, and a flowmeter before being mixed with an equal volume of carbon monoxide. The diluted blend now enters the detector and is analyzed as was the exhaust sample. The portion of the diluted blend which was not pumped out of the chamber flows through a quartz furnace (operating at 480°C) and through a nitric acid scrubber before being vented into the room air. By comparing the signal from this diluted blend with that of the exhaust sample, the concentration of nickel carbonyl in exhaust can be determined. Figure 5 shows the detector, sampling system, and the dilution system.

CALCULATIONS

The concentration of nickel carbonyl can be determined by comparing the peak height of the sample with the peak height of the calibration blend. Since the detector is linear in the region of interest, the concentration of the sample can be found by use of the following equation:

$$\frac{H_{std}}{C_{std}} = \frac{H_{sam}}{C_{sam}}$$

where H_{std} = the peak height of nickel carbonyl in the diluted calibration blend

C_{std} = the concentration of nickel carbonyl in the diluted calibration blend

H_{sam} = the peak height of the nickel carbonyl in the sample

C_{sam} = the unknown concentration of nickel carbonyl in the exhaust sample

Solving for C_{sam} gives:

$$C_{sam} = \frac{H_{sam} \times C_{std}}{H_{std}}$$

Example

A bag sample was taken from the exhaust stream of a vehicle during a driving cycle. The peak height due to the diluted calibration blend of nickel carbonyl was 32 units and the blend had a concentration of 0.3 ppb. The peak height for nickel carbonyl in the sample was 19 units. The concentration of nickel carbonyl in the exhaust is calculate as follows:

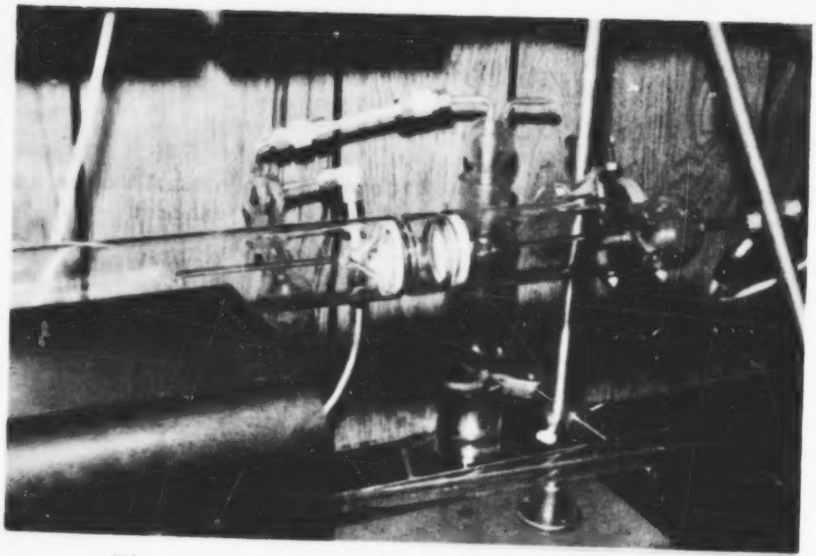

Figure 4. Glass dilution chamber.

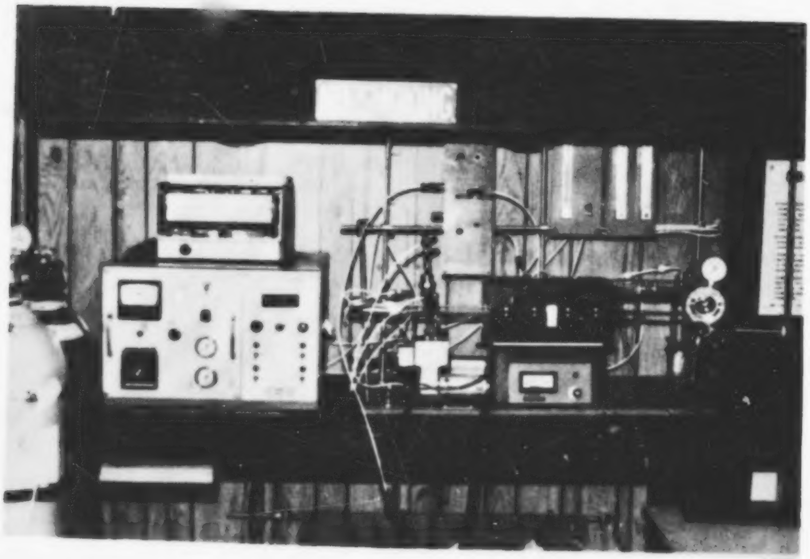

Figure 5. Chemiluminescent detector, sampling and dilution system.

$$C_{sam} = \frac{H_{sam} \times C_{std}}{H_{std}}$$

$$C_{sam} = \frac{19 \times 0.3 \text{ ppb}}{32}$$

$$C_{sam} = 0.18 \text{ ppb}$$

Note: The sample calculation is presented as an example only and is not necessarily representative of expected values in exhaust.

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APPENDIX K

AMMONIA PROCEDURE

THE MEASUREMENT OF AMMONIA IN DILUTE EXHAUST

Ammonia in automotive exhaust can be measured in the protonated form NH_4^+, after collection in dilute H_2SO_4. The acidification is carried out in a glass impinger maintained at ice bath temperatures (0-5°C). A sample from the impinger is then analyzed for ammonia in the Ion Chromatograph and the concentration in the exhaust is calculated by comparison to a standard.

EQUIPMENT

The equipment section lists the equipment used in the ammonia procedure. It is divided into four sections corresponding to each major division in the procedure: Sampling, Analysis, Water Filtration and Sample Preparation. For convenience the item, manufacturer, model number and any additional pertinent information are included.

Sampling

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/24 bottle joints.
2. Flowmeters, Brooks Instrument Division, Model 1555, R-2-15-C, sapphire ball, 0-5 lit/min range, graduated 0-15.
3. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.
4. Digital readout for dry gas meter.
5. Sample pump, Thomas, Model #106 CA18, 4 lit/min free flow capacity.
6. Drying tube, Analabs Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.
7. Teflon tubing, United States Plastic Corporation, 1/4" OD × 1/8" ID and 5/16" OD × 3/16" ID.
8. Teflon solenoid valve, The Fluorocarbon Company, Model #DV2-144N CA1.
9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps and connectors, etc.
10. Miscellaneous electrical switches, lights, wiring, etc.

11. Regulating valve, Nupro 4MG, stainless steel.

12. Iron/constantan Type J, Thermo Sensors Corporation, single thermocouple, 1/4" OD stainless steel metal sheath.

13. Six channel digital thermometer, Analog Devices, Model #2036/J/1.

14. 30 mℓ polypropylene sample storage bottles, Nalgene Labware, Catalog #2006-0001.

Analysis

1. Dionex Model 10 Ion Chromatograph.

2. Multivoltage recorder, Texas Instruments, Model #PS02W6A.

3. Polyethylene cubitainers, Cole Parmer Instrument Company, Catalog #6100-20, 1 gallon.

Water Filtration

1. Filtration apparatus, Millipore, Model #XX 1504700.

2. Filters, Millipore, Model #GSWP04700, 0.22 micron pore size.

Sample Preparation

1. 3 cc disposable syringes, Becton-Dickson, Model #5585.

2. 15 mℓ disposable polypropylene cups, Cole-Parmer Instrument Company, Catalog #6006-10.

3. Class A, 1 mℓ volumetric pipets.

4. Class A, 2 mℓ volumetric pipets.

5. Class A, 3 mℓ volumetric pipets.

6. Class A, 4 mℓ volumetric pipets.

7. Class A, 5 mℓ volumetric pipets.

8. Class A, 10 mℓ volumetric pipets.

9. Class A, 20 mℓ volumetric pipets.

10. Class A, 25 mℓ volumetric pipets.

11. Class A, 50 mℓ voluemtric pipets.

12. Class A, 100 mℓ volumetric pipets.

13. Class A, 100 mℓ volumetric flasks.

14. Class A, 1000 mℓ volumetric flasks.

15. Class A, 2000 mℓ volumetric flasks.

16. Mohr pipet, 1 mℓ graduated 1/10.

LIST OF REAGENTS

The reagents used in the analysis of ammonia are presented in this section. In addition to the function of each reagent, the purity, manufacturer and catalog number are also listed.

1. Water-deionized and filtered through a 0.22 micron filter.

2. Standard
   Ammonium sulfate, $(NH_4)_2SO_4$, formula weight = 132.146, ACS analytical reagent grade, granular, J. T. Baker Chemical Co. #0792.

3. Absorbant
   Sulfuric acid, H_2SO_4, formula weight = 98.08, ACS analytical reagent grade, Mallinckrodt #2876.

4. Eluent
   Nitric acid, HNO_3, formula weight = 63.01, ACS analytical reagent grade (Ultrex), J.T. Baker, #1-4801.

5. Regenerant
   Sodium hydroxide, NaOH, formula weight = 40.00, ACS analytical reagent grade, pellets, Mallinckrodt #7708.

PREPARATION OF REAGENTS.

The water used in making all solutions and dilutions is prepared by filtering deionized water through a 0.22 micron filter. After filtration the water is stored in polyethylene bottles.

Standard $(NH_4)_2SO_4$

The stock solution is prepared by diluting 0.3660g of $(NH_4)_2SO_4$ to 1000 mℓ with water. This yields a solution with a concentration of 100 $\frac{\mu g\ HN^+_4}{m\ell}$. Less concentrated standards are made up by diluting portions of of the stock solution to 100 mℓ with water using volumetric glassware.

Absorbing Solution (0.01N H_2SO_4)

The absorbant is prepared by diluting 20.0 mℓ of the certified 1.000N sulfuric acid to 2000 mℓ with water.

Eluent (0.0075N HNO_3*

A 1N HNO_3 stock solution is prepared by diluting 62.5 mℓ of concentrated nitric acid to 1000 mℓ with water. The eluent is prepared by further diluting 15 mℓ of the stock solution to 2000 mℓ with water.

Regenerant (0.5N NaOH)*

40.00g of NaOH is dissolved in water in a 2 liter volumetric flask and brought up to volume.

* 4 liters of each of these solutions are prepared and stored in labeled polyethylene cubitainers.

SAMPLING SYSTEM

As seen in the schematic of the ammonia sampling system (Figure 1) dilute automotive exhaust is diverted from the CVS to the sampling probe. An on-off solenoid valve controls the gas flow to the system. If the valve is open a Thomas sample pump equipped with a molecular sieve-silica gel dryer pulls the exhuast at 2 lit/min through two bubblers containing 25 mℓ of 0.01N H_2SO_4. The reaction converting NH_3 to NH_4^+ proceeds in the 2 tapered tip bubblers at ice bath temperatures (0-5°C). After acidification the gas flow, which proceeds through the Singer dry gas meter, is controlled by a Nupro regulating valve and is measured by a Brooks Flowmeter. Digital readouts for the ice bath temperature (°F) and the dry gas meter volume (ft^3) are provided. Figure 2 shows several views of the ammonia sampling system.

PROCEDURE

Ammonia in exhaust is collected in two bubblers connected in series each containing 25 mℓ of 0.01N H_2SO_4. These two bubblers trap 99+ percent of the ammonia. After the acidification of ammonia which takes place at ice bath temperatures (0-5°C), the samples are stored in polypropylene bottles. The samples are then ready for NH_4^+ analysis on the ion chromatograph (pictured in Figure 3). Approximately 2 mℓ of sample is loaded into the 0.1 mℓ sample loop and injected into the eluent stream. Separation of ions occurs in the separator (analytical) column and the background conductance of the eluent (0.0075N HNO_3) is neutralized in the suppressor column. The 9 x 250 mm glass cation suppressor column is packed with AG 1- X10, a strong base ion exchange resin in the hydroxide form. A patented resin containing a sulfonic acid cation exchanger is packed into the 6 x 250 mm glass separator column and the 3 x 150 mm precolumn. After the cations are separated in the analytical column they pass into the suppressor column in the diulte nitric acid eluent. The hydroxide form of the suppressor resing neutralizes the acid and then converts the cations to their hydroxides.

$$HNO_3 + \text{Resin} - OH \rightleftharpoons \text{Resin} - NO_3 + H_2O$$

$$\text{Cation} + NO_3^- + \text{Resin} - OH \rightleftharpoons \text{Resin} - NO_3 + \text{Cation}^{+-}OH$$

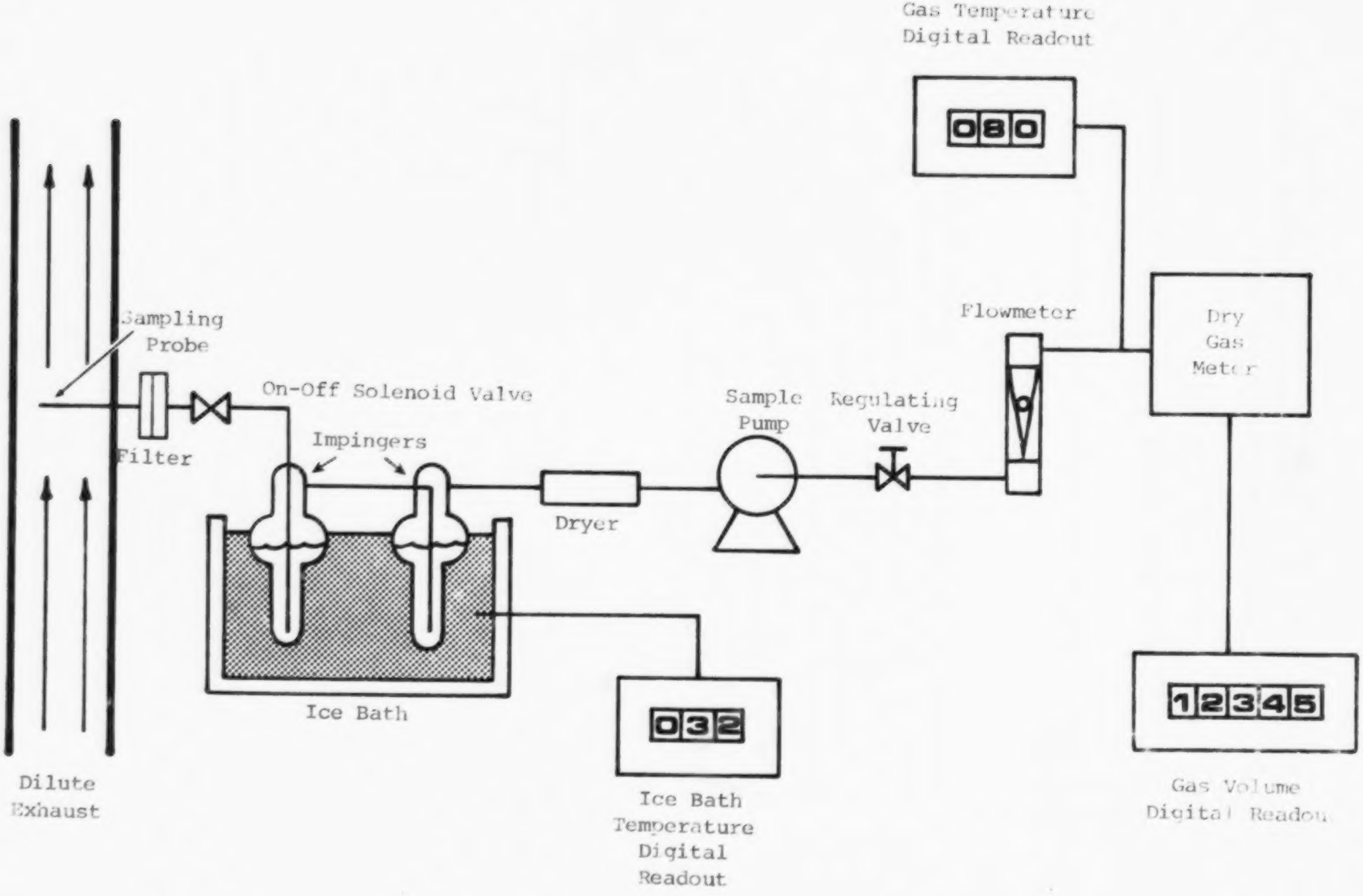
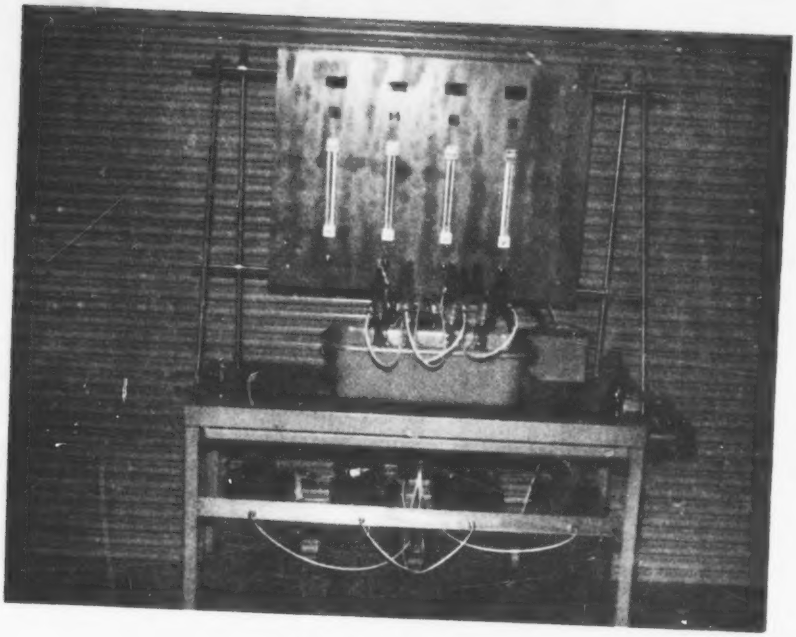
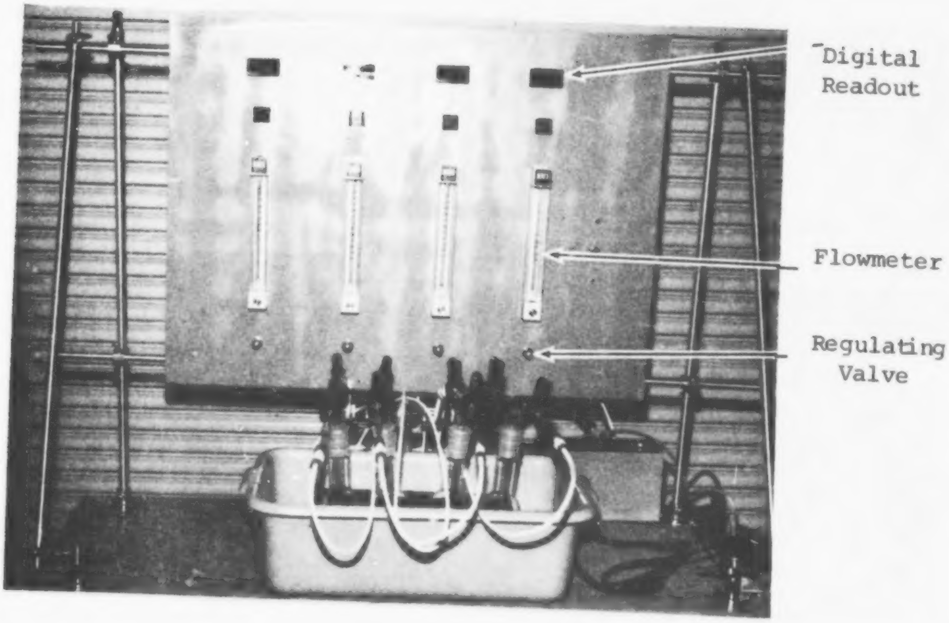

Gas Temperature
Digital Readout
080
Sampling
Probe
On-Off Solenoid Valve
Flowmeter
Dry
Gas
Meter
Sample
Pump
Regulating
Valve
Impingers
Filter
Dryer
Ice Bath
032
1 2 3 4 5
Dilute
Exhaust
Ice Bath
Temperature
Digital
Readout
Gas Volume
Digital Readout

Figure 1. NH_3 sample collection flow schematic.

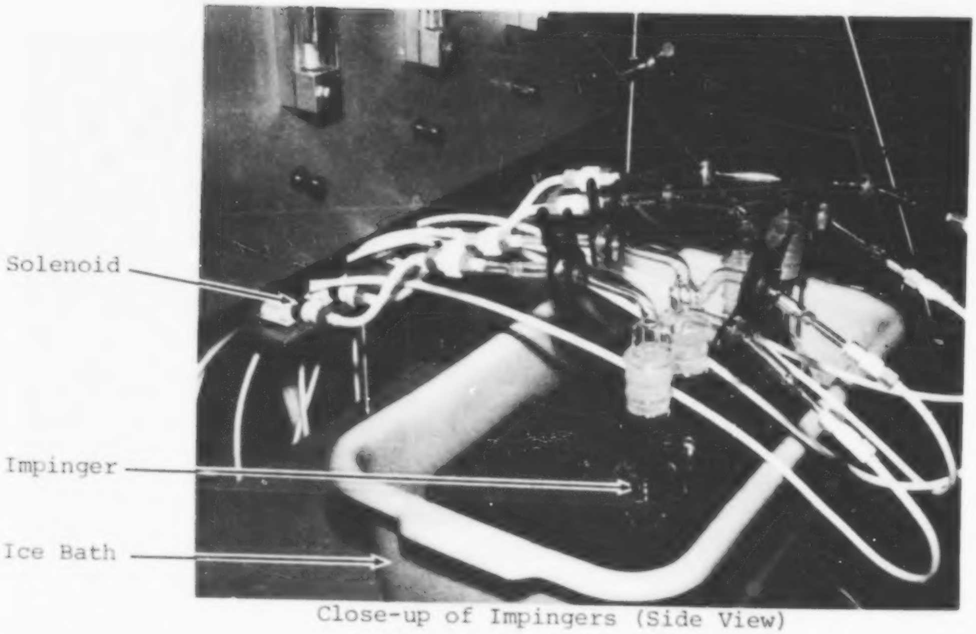


Front View

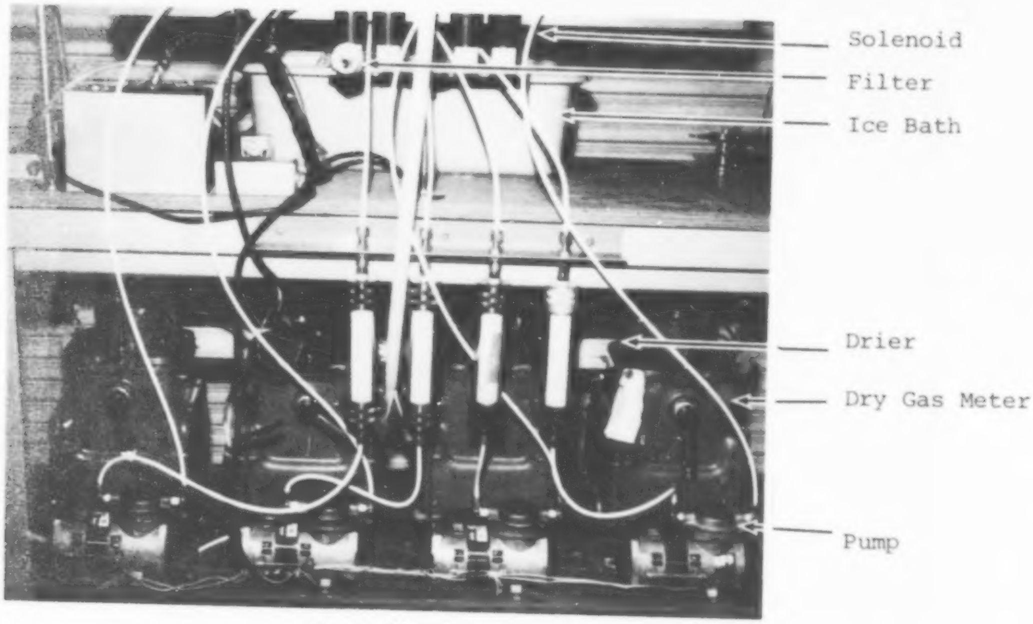

Digital
Readout
Flowmeter
Regulating
Valve

Close-up of Upper Front

Figure 2. Ammonia sampling system.


Solenoid
Impinger
Ice Bath

Close-up of Impingers (Side View)


Solenoid
Filter
Ice Bath
Drier
Dry Gas Meter
Pump

Rear View

Figure 2 (Cont'd). Ammonia sampling system.

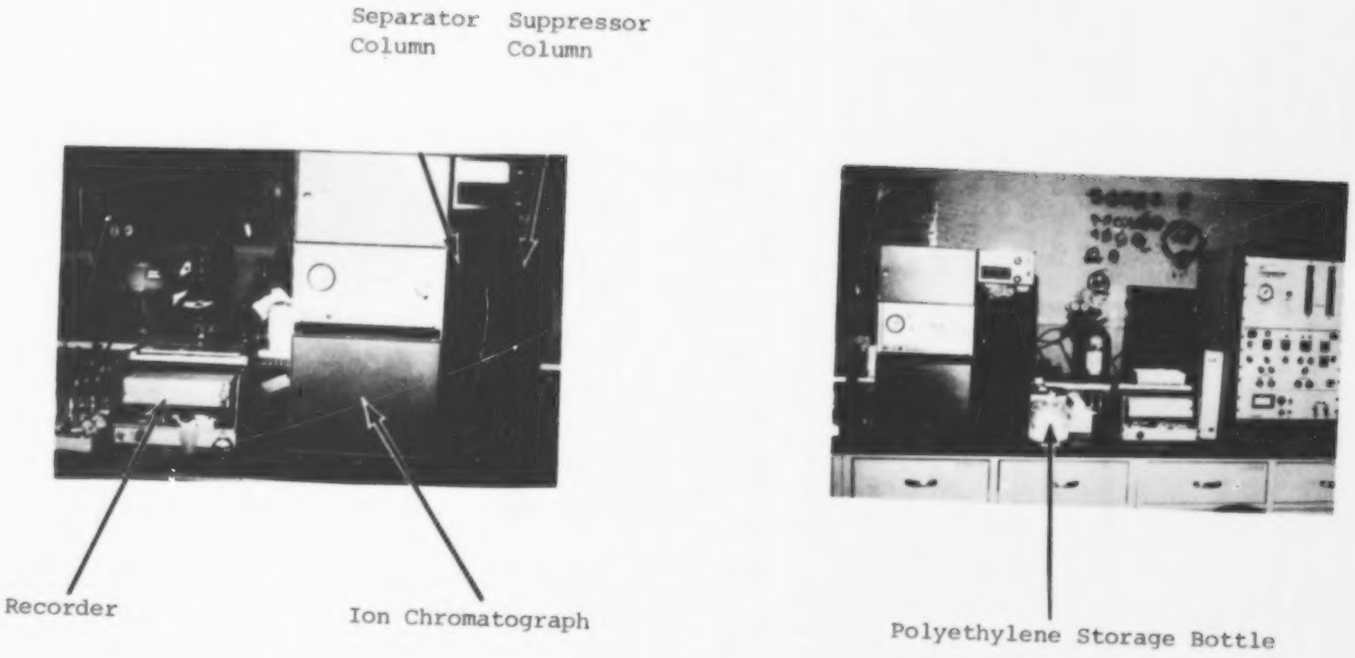

Separator Column
Suppressor Column
Recorder
Ion Chromatograph
Polyethylene Storage Bottle

Figure 3. NH_3 Ion Chromatograph.

The conductivity cell produces a signal for the species of interest, NH_4OH, but doesn't "see" the neutralized eluent, deionized water. Conductance is interpreted as a recorder trace (chromatogram) or as peak area by the Hewlett-Packard 3354 computer system. Figure 4 depicts the analysis flow schematic of the entire ammonia procedure. Two chromatograms produced by the analysis of a sample and a standard are shown if Figures 5 and 6. After the 12-20 minute analysis the collection conditions and areas of sample and standard are used to compute NH_3 concentration from the Hewlett Packard 65 program. This is then recorded on a data sheet.

CALCULATIONS

The purpose of this procedure is to determine the concentration of ammonia in automotive exhaust. To do this ammonia first needs to be converted to the protonated form, NH_4^+, which can then be directly measured on the ion chromatograph. The calculations involve correcting the measured concentration of NH_4^+ to NH_3 at a desired temperature and pressure. These calculations are carried out in a minimum amount of time by using a Hewlett-Packard 65 calculator program. A copy of the program is shown in Figure 7. Information from the data sheet (Figure 8) is entered into the calculator and the ammonia concentration in $\frac{\mu g\ NH_3}{m^3}$ and ppm NH_3 is computed. For illustration, two examples using information from the data sheet will be included at the end of this section.

The first step in the derivation of the equation for the calculation of ammonia concentration involves comparison of the sample to a standard of known concentration. The standard with peak size closest to that of the sample is the one chosen.

$$\frac{PA_{st}}{C_{st}} = \frac{PA_{sa}}{C_{sa}} \qquad\qquad C_{sa} = \frac{PA_{sa} \times C_{st}}{PA_{st}}$$

where PA_{st} = peak area of the standard

PA_{sa} = peak area of the sample

C_{st} = concentration of the standard $(\frac{\mu g\ NH_4^+}{m\ell})$

C_{sa} = concentration of the sample $(\frac{\mu g\ NH_4^+}{m\ell})$

This equation gives the concentration of NH_4^+ in the sample. To convert to to $\frac{\mu g\ NH_3}{m\ell}$ the ratio of the formula weight of NH_3 to NH_4^+ needs to be multiplied by C_{sa}.

$$C_{sa},\ \frac{\mu g\ NH_4^+}{m\ell} \times \frac{17.03(\frac{\mu g\ NH_3}{\mu\ mole})}{18.04(\frac{\mu g\ NH_4^+}{\mu\ mole})} = 0.944\ \ C_{sa},\ \frac{\mu g\ NH_3}{m\ell}$$

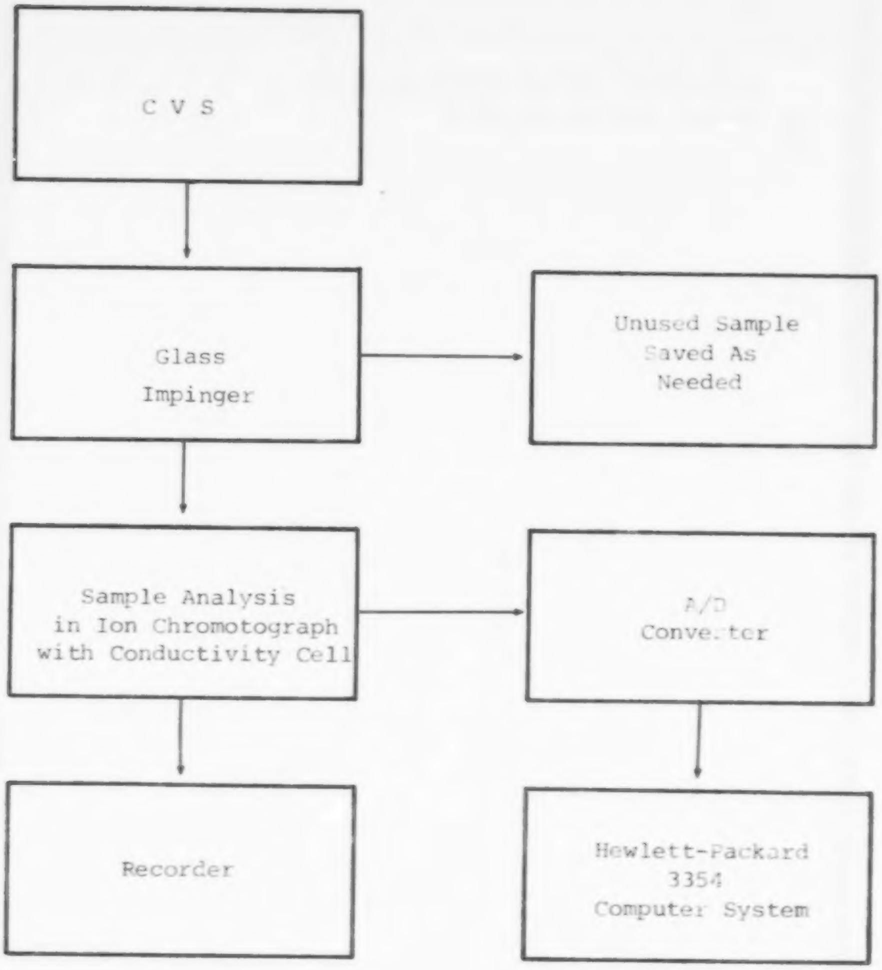
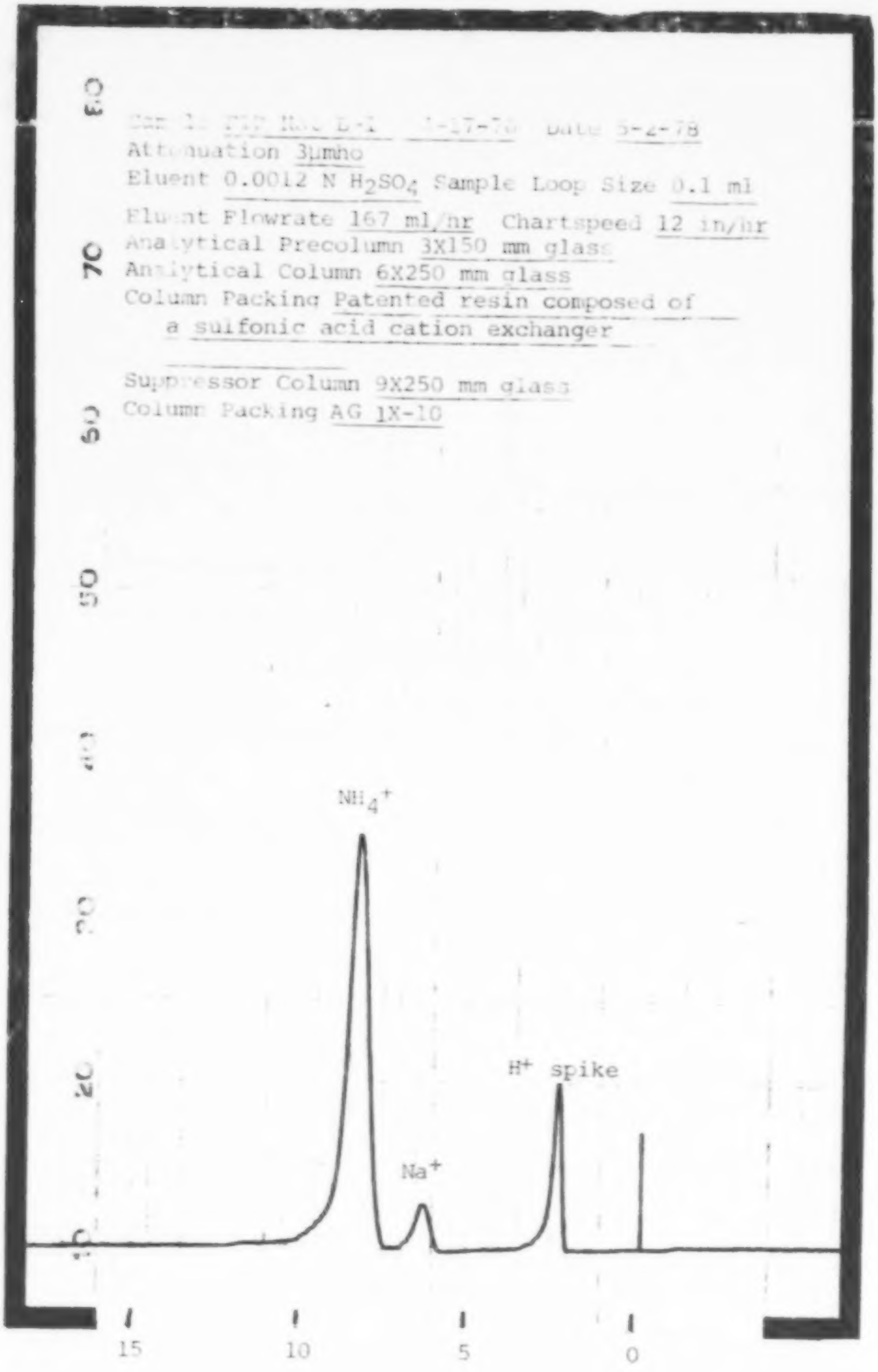
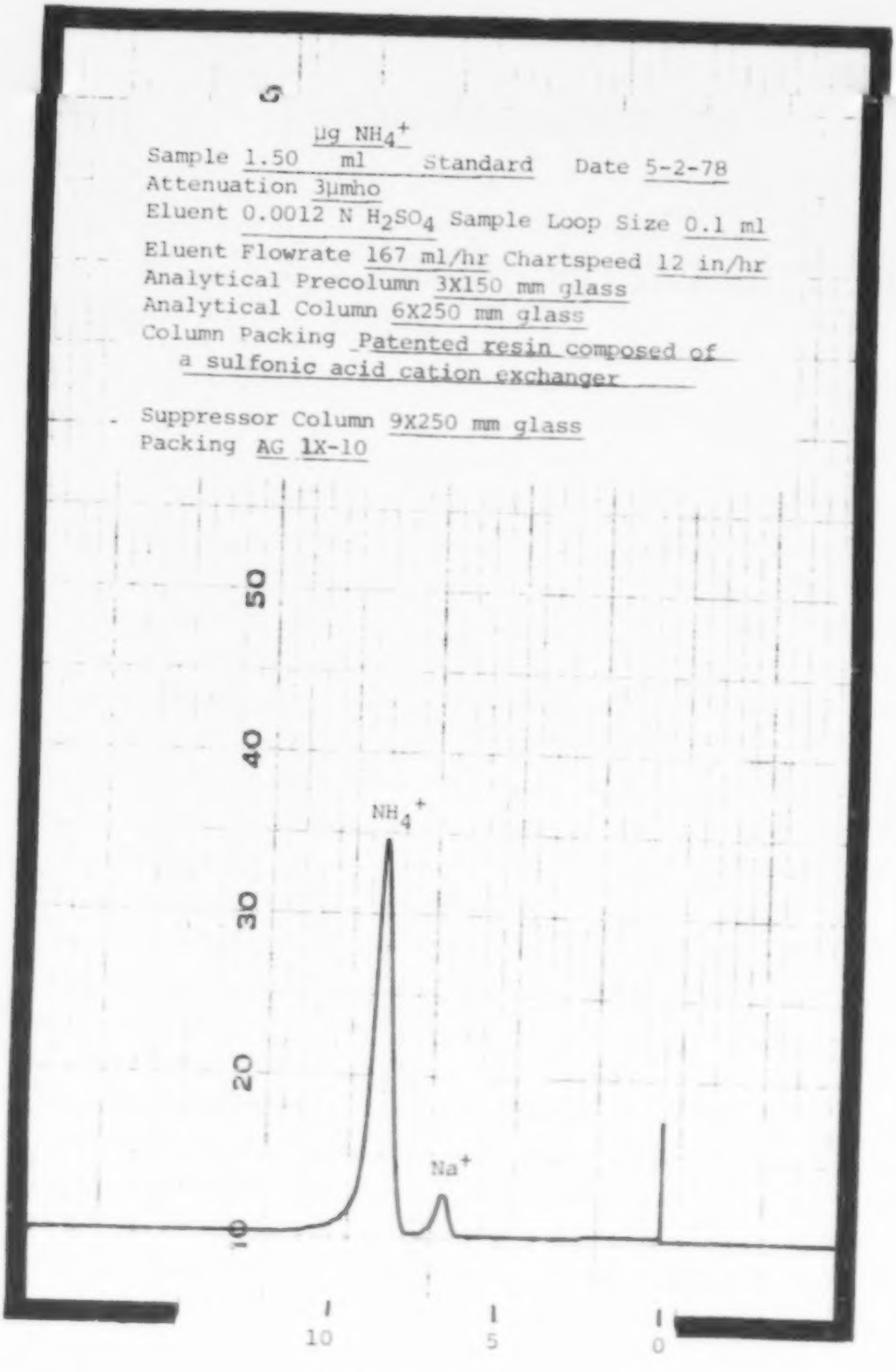

C V S
Glass Impinger
Unused Sample Saved As Needed
Sample Analysis in Ion Chromotograph with Conductivity Cell
A/D Converter
Recorder
Hewlett-Packard 3354 Computer System

Figure 4. NH_3 analysis flow schematic.



[illegible] -17-78 Date 5-2-78
Attenuation 3μmho
Eluent 0.0012 N H_2SO_4 Sample Loop Size 0.1 ml
Eluent Flowrate 167 ml/hr Chartspeed 12 in/hr
Analytical Precolumn 3X150 mm glass
Analytical Column 6X250 mm glass
Column Packing Patented resin composed of a sulfonic acid cation exchanger
Suppressor Column 9X250 mm glass
Column Packing AG 1X-10

Figure 5. Sample chromatogram.



Sample 1.50 μg NH_4^+/ml Standard Date 5-2-78

Attenuation 3μmho

Eluent 0.0012 N H_2SO_4 Sample Loop Size 0.1 ml

Eluent Flowrate 167 ml/hr Chartspeed 12 in/hr

Analytical Precolumn 3X150 mm glass

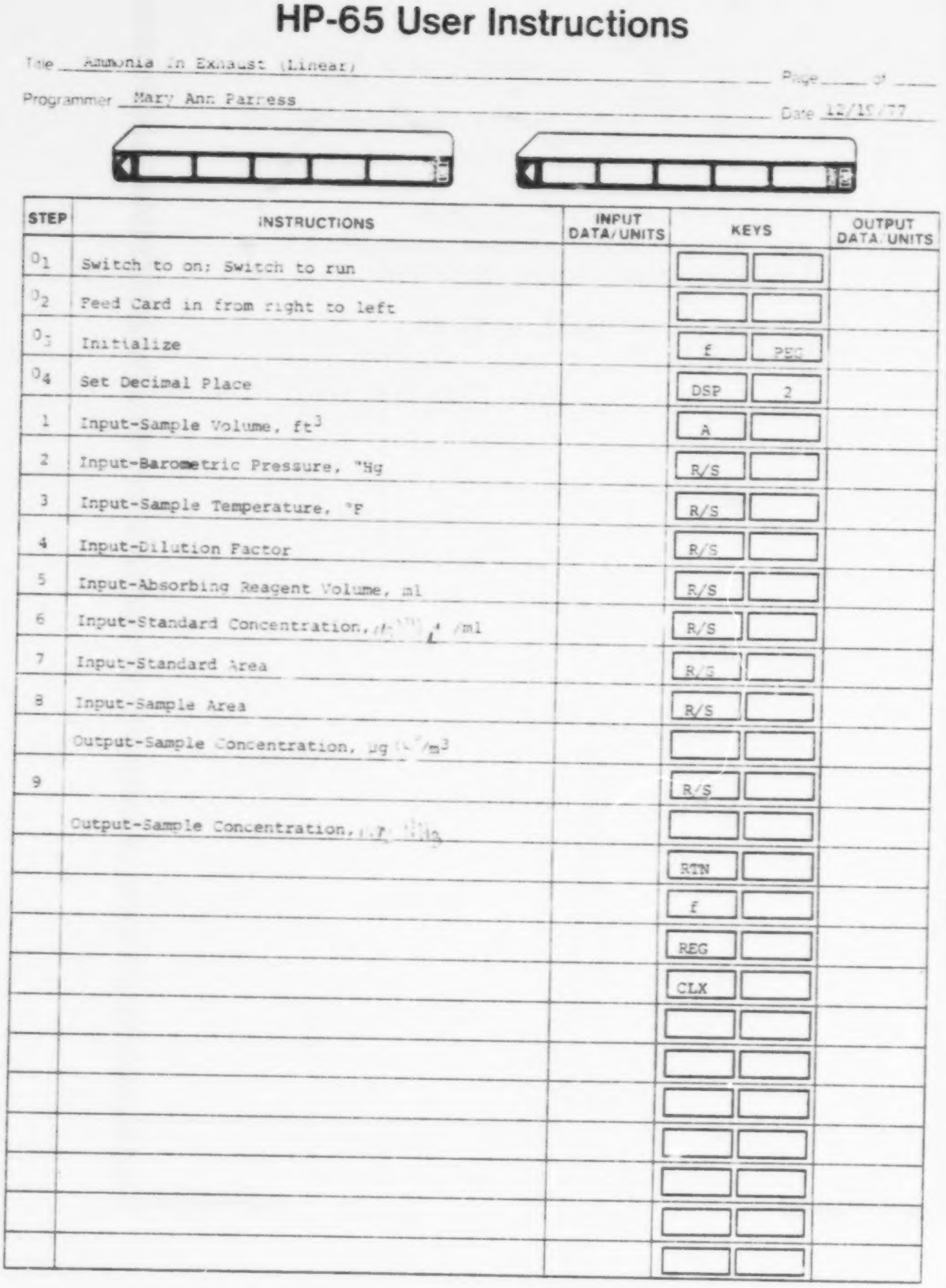
Analytical Column 6X250 mm glass

Column Packing Patented resin composed of a sulfonic acid cation exchanger

Suppressor Column 9X250 mm glass

Packing AG 1X-10

Figure 6. Standard Chromatogram.



HP-65 User Instructions

Title Ammonia In Exhaust (Linear) Page ____ of ____

Programmer Mary Ann Parress Date 12/19/77

STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on; Switch to run				
0_2	Feed Card in from right to left				
0_3	Initialize		f	REG	
0_4	Set Decimal Place		DSP	2	
1	Input-Sample Volume, ft^3		A		
2	Input-Barometric Pressure, "Hg		R/S		
3	Input-Sample Temperature, °F		R/S		
4	Input-Dilution Factor		R/S		
5	Input-Absorbing Reagent Volume, ml		R/S		
6	Input-Standard Concentration, [illegible] /ml		R/S		
7	Input-Standard Area		R/S		
8	Input-Sample Area		R/S		
	Output-Sample Concentration, µg [illegible]/m^3				
9			R/S		
	Output-Sample Concentration, [illegible]				
			RTN		
			f		
			REG		
			CLX		

Figure 7. HP-65 Program.

HP-65 Program Form

Title Ammonia In Exhaust (Linear) Page ____ of ____

SWITCH TO W/PRGM PRESS f PRGM TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23	
A	11	Input-Sample Vol. ft^3
3		
5		
.	83	
3		
1		
÷	81	
5		
2		
8		
X	71	
2		
9		
.	83	
9		
2		
÷	81	
R/S	84	Input-Barometer, "Hg
X	71	
STO 1	33 01	
R/S	84	Input-Sample Temp. °F
4		
6		
0		
+	61	
RCL 1	34 01	
g x≷y	35 07	
÷	81	
g 1/X	35 04	
R/S	84	Input-Dilution Factor
X	71	
R/S	84	Input-Abs. Soln. Vol. ml
X	71	
R/S	84	Input-Stand. Conc. $\mu gSO_4^{-2}/ml$
X	71	
R/S	84	Input-Stand. Area
÷	81	
R/S	84	Input-Sample Area
X	71	
0		
.	83	
9		
4		
4		
X	71	
R/S	84	
0		
.	83	
0		

KEY ENTRY	CODE SHOWN	COMMENTS
0		
1		
4		
1		
X	71	
R/S	84	
RTN		

REGISTERS

R1 ____

R2 ____

R3 ____

R4 ____

R5 ____

R6 ____

R7 ____

R8 ____

R9 ____

LABELS

A ____
B ____
C ____
D ____
E ____
0 ____
1 ____
2 ____
3 ____
4 ____
5 ____
6 ____
7 ____
8 ____
9 ____

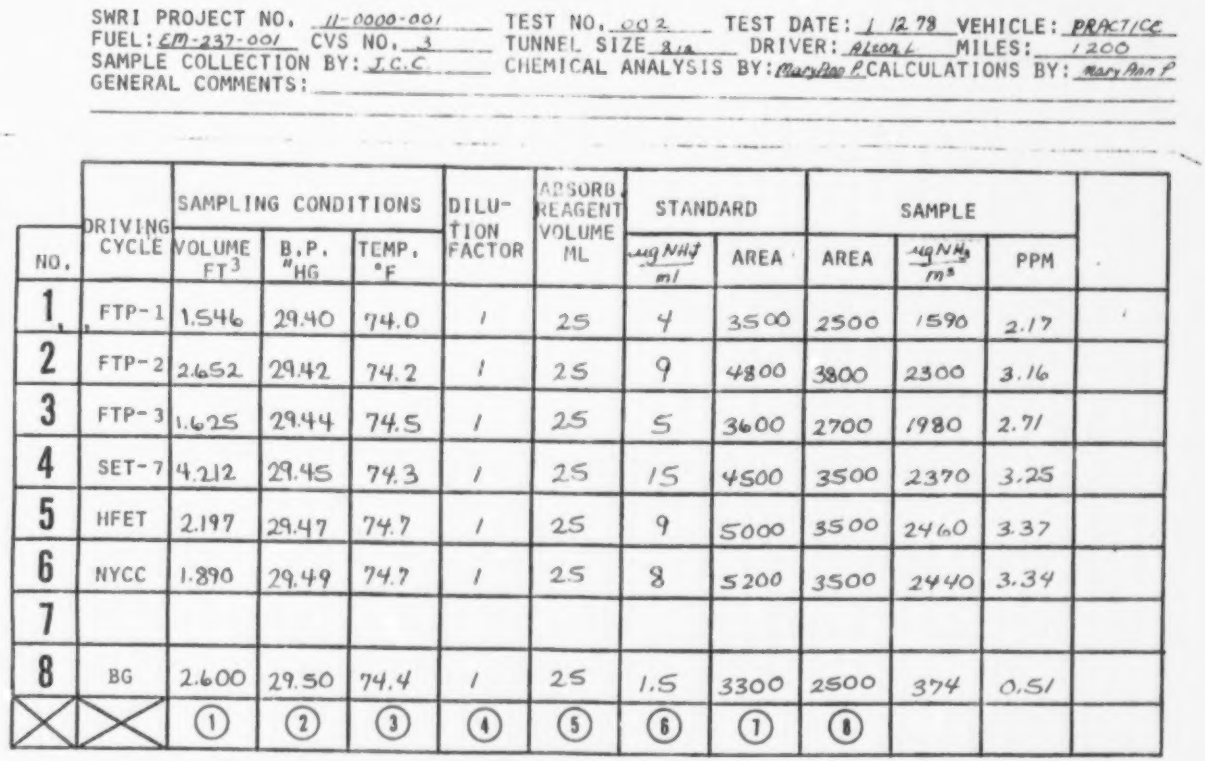
FLAGS

1 ____

2 ____

TO RECORD PROGRAM INSERT MAGNETIC CARD WITH SWITCH SET AT W/PRGM

Figure 7 (Cont'd). HP-65 Program.



SWRI PROJECT NO. 11-0000-001 TEST NO. 002 TEST DATE: 1 12 78 VEHICLE: PRACTICE
FUEL: EM-237-001 CVS NO. 3 TUNNEL SIZE 8 in DRIVER: ALeon L MILES: 1200
SAMPLE COLLECTION BY: J.C.C CHEMICAL ANALYSIS BY: MaryAnn P. CALCULATIONS BY: MaryAnn P
GENERAL COMMENTS:

NO.	DRIVING CYCLE	SAMPLING CONDITIONS			DILUTION FACTOR	ABSORB. REAGENT VOLUME ML	STANDARD		SAMPLE			
		VOLUME FT^3	B.P. "HG	TEMP. °F			$\mu g\ NH_3/ml$	AREA	AREA	$\mu g\ NH_3/m^3$	PPM	
1	FTP-1	1.546	29.40	74.0	1	25	4	3500	2500	1590	2.17	
2	FTP-2	2.652	29.42	74.2	1	25	9	4800	3800	2300	3.16	
3	FTP-3	1.625	29.44	74.5	1	25	5	3600	2700	1980	2.71	
4	SET-7	4.212	29.45	74.3	1	25	15	4500	3500	2370	3.25	
5	HFET	2.197	29.47	74.7	1	25	9	5000	3500	2460	3.37	
6	NYCC	1.890	29.49	74.7	1	25	8	5200	3500	2440	3.34	
7												
8	BG	2.600	29.50	74.4	1	25	1.5	3300	2500	374	0.51	
☒	☒	①	②	③	④	⑤	⑥	⑦	⑧			

Figure 8. NH_3 Data Sheet.

The next step involves the determination of the amount of NH_3 collected in the bubbler. This is obtained by multiplying the volume of absorbant (absorb. vol.) and the dilution factor (DF) by the concentration of ammonia collected.

$$0.944\ C_{sa},\ \frac{\mu g\ NH_3}{m\ell} \times \text{absorb. vol, } m\ell \times DF = \mu g\ NH_3$$

To find the concentration of NH_3 in exhaust the volume of gas collected first needs to be corrected to the specified temperature and pressure (68°F= 528°R, 29.92 in Hg). The volume as read from the digital readout in cubic feet needs to be changed to cubic meters.

$$\frac{\text{VOL, ft}^3}{35.31\ \frac{ft^3}{m^3}} \times \frac{29.92 \text{ in Hg}}{\text{B.P., in Hg}} \times \frac{(\text{TEMP, }°F + 460)}{528°F}$$

where VOL = volume of gas collected, ft^3

B.P. = collection pressure, in Hg

TEMP = collection temperature, °F

The concentration of NH_3 can be calculated by dividing $\mu g\ NH_3$ by the volume of gas.

$$\frac{0.944 \times \dfrac{C_{st},\ \frac{\mu g\ NH_4^+}{m\ell} \times PA_{sa}}{PA_{st}} \times \text{absorb. vol, } m\ell \times DF}{\dfrac{\text{VOL, ft}^3}{35.31\ \frac{ft^3}{m^3}} \times \dfrac{\text{B.P., in Hg}}{29.92 \text{ in Hg}} \times \dfrac{528°R}{(\text{TEMP, }°F + 460)}}$$

$$= \frac{0.944 \times C_{st},\ \frac{\mu g\ NH_4^+}{m\ell} \times PA_{sa} \times \text{absorb. vol, } m\ell \times DF}{\text{VOL, ft}^3 \times PA_{st}} \times \frac{35.31\ \frac{ft^3}{m^3} \times 29.92 \text{ in Hg} \quad (\text{TEMP, }°F + 460)}{\text{B.P., in Hg} \times 528°R}$$

$$= \frac{\mu g\ NH_3}{m^3}$$

This concentration can also be expressed in ppm NH by taking into consideration the density of the gas at the desired conditions (68°F, 29.92 in Hg). The fifth edition of the Matheson Gas Data Book lists the specific gravity of ammonia gas at 70°F and 1 atm pressure as 1.411 ℓ/g. The inverse of the specific gravity gives a density of 0.709 $\frac{g}{\ell}$. If the volume of 1ℓ of gas is corrected for temperature,

$$V = 1\ \ell \times \frac{528\,°F}{(70°F + 460)} = 0.966\ \ell,$$

it can be divided into the weight of the gas to give the density at 68°F.

$$\frac{0.709\ g}{0.996\ \ell} = 0.712\ \frac{g}{\ell} = 712\ \frac{\mu g}{m\ell}$$

$$= 0.00141\ \frac{m\ell}{\mu g\ NH_3}$$

When the inverse of density is multiplied by the concentration in $\frac{\mu g\ NH_3}{m^3}$, the concentration is given in ppm NH_3.

$$\frac{\mu g\ NH_3}{m^3} \times 0.00141\ \frac{m\ell}{\mu g\ NH_3} = \frac{m\ell}{m^3} = \text{ppm } NH_3$$

Sample Calculation

The two examples will be calculated from information recorded on the data sheet. This information does not necessarily represent actual experimental data but serves as a means of confirming calcuations done by hand with those done with the Hewlett Packard Calculator.

Example 1

Assume that in the FTP-2 driving cycle that 2.652 ft^3 of dilute exhaust is collected in 25 mℓ of 0.01 N H_2SO_4 at 74.2 °F and 29.42 in Hg. When the undiluted sample is injected into the Ion Chromatograph it yields a peak area of 3800 counts. A 9 $\frac{\mu g\ NH_4^+}{m\ell}$ standard similarly injected produces an area of 4800 counts.

The equation needed to calculate the concentration of ammonia follows:

$$\frac{\mu g\ NH_3}{m^3} = \frac{0.944 \times C_{st},\ \frac{\mu g\ NH_4^+}{m\ell} \times PA_{sa} \times \text{absorb. vol, } m\ell}{VOL,\ ft^3 \times PA_{st}} \times$$

$$\frac{DF \times 35.31\ ft^3/m^3 \times 29.92\ \text{in Hg} \times (TEMP,\ °F + 460)}{B.P.,\ \text{in Hg} \times 528\ R}$$

$$= \frac{0.944 \times 9 \times 3800 \times 25 \times 1 \times 35.31 \times 29.92 \times (74.2 + 460)}{2.652 \times 4800 \times 29.42 \times 528}$$

$$= 2300 \frac{\mu g\ NH_3}{m^3}$$

$$\text{ppm } NH_3 = 2300 \times 0.00141 = 3.24 \text{ ppm } NH_3$$

Example 2

Assume that 1.890 ft^3 of dilute automotive exhaust was collected in 25 mℓ of 0.01 N H_2SO_4 during the NYCC driving cycle. The sampling conditions during this test were 74.7°F and 29.49 in Hg. When the undiluted sample was injected into the ion chromatograph the peak produced had an area of 3500 counts. When an 8 $\frac{\mu g\ NH_4^+}{m\ell}$ standard was injected it produced an area of 5200 counts.

The same equations in Example one are used to give concentrations of NH_3 of 2400 $\frac{\mu g\ NH_3}{m^3}$ and 3.34 ppm NH_3.

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APPENDIX L

SULFATE PROCEDURE

THE MEASUREMENT OF SOLUBLE SULFATE IN EXHAUST

As used by

Department of Emissions Research
Southwest Research Institute

Developed by

Mobile Source Emissions Research Branch
Environmental Sciences Research Laboratory
Environmental Protection Agency
Research Triangle Park, North Carolina

January 1977

Determination of Soluble Sulfates in Automobile Exhaust by Automated HPLC Modification of the Barium Chloranilate Method

by

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1. Principle and Applicability

1.1 Principle

Automotive exhaust is vented into a dilution tunnel where it is mixed with a flowing stream of cool filtered air. In the tunnel, the SO_3 reacts rapidly with water in the exhaust to form sulfuric acid aerosols. The aerosols are allowed to grow to filterable size range and are collected on fluorocarbon membrane filter downstream of the tunnel via isokinetic probes mounted in the flowing aerosol stream. Particulate sulfate salts are collected as well.

Sulfuric acid on the filter is converted to ammonium sulfate by exposure to ammonia vapor. The soluble sulfates are leached from the filter with a measured volume of 60% isopropyl alcohol - 40% water solution (60% IPA). A fixed volume of the sample extract is injected into a high pressure liquid chromatograph (HPLC) and pumped through a column of strong cation exchange resin in Ag^+ form to scrub out the halides (Cl^-, Br^-), then through a column of strong cation exchange resin in H^+ form to scrub out the cations and convert the sulfate to sulfuric acid and finally through a reactor column of barium chloranilate crystals to precipitate out barium sulfate and release the highly UV absorbing chloranilate ions. The amount of chloranilate ions released is equivalent to the sulfate in the sample and is measured by a sensitive liquid chromatograph UV detector at 310-313 nanometers. All the reactions and measurement take place in a flowing stream of 60% IPA. The scrubber and reactor columns also function as efficient filter media for any solid reaction products formed during passage of the sample through the column system.

1.2 Applicability

The method as specified is applicable to the determination of soluble sulfates in automobile exhaust. It may be used for the analysis of sulfates in samples where the sulfates can be leached out with water or aqueous IPA solution. Aqueous extracts must be made up to 60% IPA before they can be analyzed.

2. Interferences

2.1 Cationic interferences are removed by the strong cation exchange resin in H^+ form.

2.2 Halide interferences are removed by the strong cation exchange resin in Ag^+ form. Other anions which form insoluble salts with silver are also removed.

2.3 Sulfite is measured quantitatively as sulfate.

2.4 Anions which form strong acids after passage through the cation exchanger in H^+ form interfere positively. Nitrate at 60 μgs/mℓ gives an apparent sulfate response corresponding to 8 μgs/mℓ.

2.5 Presence of anionic interference is manifested by a negative peak immediately preceding the positive apparent sulfate peak.

2.6 Organics with absorption bands at 310-313 will interfere positively.

3. Range, Sensitivity and Precision

3.1 The absolute amount of $SO_4^=$ normally injected into the system is between 0 - 12.5 μgs. For a typical sample injection volume of 0.5 mℓ, this translates to a concentration working range of 0 - 25 μgs/mℓ. Working range can be extended by using a smaller sample injection volume for concentrated samples or conversely, by using a larger injection volume for dilute samples.

3.2 Minimum detectable quantity of $SO_4^=$ is in the low nanogram range. There are commercially available liquid chromatograph UV detectors capable of detecting 5 nanograms of sulfate at a signal to noise ratio of about 5. Figure 1 shows typical recorder response for a 0.5 mℓ injection of sulfate samples at trace concentration levels (0.01 - 0.1 μgs/mℓ.

3.3 Precision better than 3% at 0.5 μg/mℓ $SO_4^=$ level and better than 2% between 1 and 20 μgs/mℓ for four repetitive runs have been attained. Table 1 and Figure 2 show typical reproducibility obtained with the automated BCA system.

4. Apparatus

A schematic of the principal components of the automated BCA set up is shown in Figure 3.

4.1 Hardware

4.1.1 Basic System

4.1.1.1 High pressure liquid chromatograph pump (LP). The pump must be capable of delivering liquids at flow rates of at least 3 mℓ/min. at pressures as high as 1200 psi. Liquid pumps capable of delivering pulseless and constant liquid flow are recommended for good quantitation. Most HPLC pumps in the market are adequate.

4.1.1.2 UV detector (D) equipped with low dead volume (8 μℓ) flow-through cell and a grating, prism or appropriate interference filter to isolate a narrow radiation band centered at 310-313 nanometers. For low noise and long life, a UV detector equipped with low pressure mercury lamp and a 313 nanometer narrow band pass interference filter is recommended.

4.1.1.3 A two position, six port, high pressure, low dead volume sample injection valve (SV). This must be equipped with interchangeable external loop (L). Two loop sizes are desirable: a 0.5 mℓ volume for the 0 - 20 μg/mℓ range and a 100 μℓ volume for 0 - 100 μgs/mℓ range. The sample valve must be equipped with an external handle for manual operation or an air actuator for remote and/or automatic operation. These valves are commercially available and have pressure ratings as high as 7000 psi.

4.1.1.4 Recorder. Must be multi-range, with chart speed as low as 10 minutes per inch. Dual channel is preferable so that chromatogram can be simultaneously recorded at two different sensitivities.

4.1.1.5 Strong cation exchange resin column ($CX-Ag^+$), 4mm I.D. by 1/4 inch O.D. by 6 inches long stainless steel column packed with chromatographic grade. Strongly acidic cation exchange resin in silver (Ag^+) form.

4.1.1.6 Strong cation exchange resin column ($CX-H^+$), 4 mm I.D. by 1/4 inch O.D. by 9 inches long stainless steel column packed with strongly acidic cation exchange resin in hydrogen (H^+) form.

4.1.1.7 Barium chloranilate column (BCA), 4 mm I.D. by 1/4 inch by 1 inch long stainless steel column packed with crystalline barium chloranilate.

4.1.1.8 1/4" to 1/16" stainless steel reducer preferably fitted with 5 micron pore size frit - for column inlet and end fittings.

4.1.1.9 1/4" to 1/4" stainless steel unions.

4.1.1.10 1/16" to 1/16" low dead volume stainless steel couplings to interconnect $CX-Ag^+$ to $CX-H^+$ to BCA columns.

4.1.1.11 1/4" and 1/16" nuts and ferrules.

4.1.1.12 Reservoir (LR) for the solvent (60% IPA).

4.1.2 Options - These items are needed for automating the basic system.

4.1.2.1 Integrator, for measuring peak areas. Recommended unit must have baseline tracking capability and possibly with built-in calculation accessory. The integrator extends useful dynamic range of detector response for a given sample loop size beyond that of the strip chart recorder.

4.1.2.2 Peristaltic pump, (PP), to draw sample from its container and load it into sample loop. Silicone pump tubing is recommended.

4.1.2.3 Automatic sampler (AS), available from commercial sources. This is needed if the number of samples to be analyzed is large and manpower is limited.

4.1.2.4 Three timer relays to control pump, sampler, injection valve and integrator and provide automatic reset for cyclic operations.

4.1.2.5 Prepackaged sampler systems for HPLC application are commercially available.

5. Principle of Operation

Solvent (60% IPA) in reservoir LR (Figure 3) is continuously pumped by an HPLC pump LP through a column of strong cation exchange resin in silver form, CX-Ag$^+$, then through a column of strong cation exchange resin in hydrogen form, CX-H$^+$, then through a reactor column of barium chloranilate, BCA, and finally through a flow-through cell of a UV detector, D, and on to waste. CX-Ag$^+$ removes the halides (Cl$^-$, Br$^-$, F$^-$) and other anions which precipitate with silver; CX-H$^+$ removes metallic cations and converts the sulfate to sulfuric acid, and the BCA reacts with the sulfate to form barium sulfate precipitate and a soluble UV absorbing dye, chloranilic acid and its ions. Background absorbance at 310 - 313 nanometers is continuously measured and monitored on a strip chart recorder.

Sample is introduced into the system without flow interruption by means of a two-way six port low dead volume sample injection valve SV. In load position "A" (see Figure 3) the peristaltic pump, PP, draws the sample from a cuvette in the automatic sampler AS and pumps it into port 4 filling external sample loop L then through port 5 to waste. (Sample loop loading may also be accomplished by pushing the sample through port 4 by means of a syringe.) The high pressure liquid flow comes in through port 1, bypasses the loop L, comes out of port 2, and continues on through the three columns and the flow-through cell of the UV detector D and on to waste

After loop L is loaded with sample, injection valve SV switches to inject position "B". The high pressure stream purges the loop and pushes the sample through the cation exchangers and then through the BCA column where the color reaction takes place. The BaSO$_4$ precipitate is retained in the column while the acid chloranilate is carried by the flowing liquid through the detector system for colorimetric measurement.

6. Apparatus

6.1 Pipette, volumetric, 1, 2, 4, 5, 8, 25, 50, 100 mℓ

6.2 Pipette, measuring, 1, 2, 5, 10 mℓ

6.3 Automatic burette, 25 mℓ

6.4 Volumetric flasks, 10, 25, 50, 100, 500, 1000, 2000 mℓ

6.5 Bottles, polypropylene, with screw caps, 30, 60, 125, 250, 500, 1000

6.6 Microbalance

6.7 Vortex test tube mixer

6.8 Centrifuge

6.9 Magnetic mixer

6.10 Magnetic bars

6.11 Graduated cylinders

6.12 Automatic dispenser pipet, 5, 10, 20 mℓ (optional)

6.13 Automatic burette, 10 mℓ (motor driven, optional)

6.14 Ammoniation chamber (Figure 5)

7. Reagents

7.1 Isopropyl alcohol (IPA), spectro quality grade or equivalent

7.2 Water, doubly deionized, distilled.

7.3 60% IPA. Add 4 parts water to 6 parts IPA by volume. Store in tightly capped bottles.

7.4 Barium chloranilate, suitable for sulfate analysis. Must be crystalline, granular, preferably with average granule length of about 200 microns. Finer particles cause excessive column pressure drop.

7.5 Cation exchange resin, chromatographic grade, strongly acidic, hydrogen form, 100 - 200 mesh.

7.6 Hydrochloric acid (4N). Add 30 mℓ concentrated hydrochloric acid to 60 mℓ of deionized water.

7.7 Ammonium sulfate, primary standard

7.8 Silver nitrate (1N). Dissolve 17 grams silver nitrate in deionized water and make up to 100 mℓ. Store in the dark in an amber colored reagent bottle.

8. Procedure

8.1 Column Preparation

8.1.1 Barium chloranilate column. In order to prepare a full column with minimum dead volume, connect two lengths of 4 mm I.D., 1/4" O.D. stainless steel tubing as shown in Figure 4 with a = 1", b = 2". Connect a small funnel to open end of B with a flexible tubing sleeve. Fill the funnel halfway with barium chloranilate and thump the tube several times or use a vibrator (i.e., electric pencil engraver) to pack the solid in the column. Continue the operation until B is completely filled. Remove the funnel and cap the open end of B with a 1/4" to 1/16" reducer fitted with 5 micron stainless steel frit. The 5 micron stainless steel frit in column A may be replaced with a stainless steel wire screen with nominal porosity of 10 microns. Connect B to the HPLC pump, connect a flexible tubing at A and direct the tubing to waste reservoir. Fill HPLC pump reservoir with 60% IPA. Activate HPLC pump according to manufacturer's instructions, set flow at 3 - 4 mℓ/min. and let solvent flow for at least 20 minutes. This procedure removes the fines which can cause background drift and at the same time compresses the barium chloranilate crystals to fill the dead volume in column A. Deactivate the HPLC pump, disconnect the composite column from the pump, then column A from the composite column. Connect a 1/4" to 1/16" reducer fitted with 5 micron frit to open end of A.

8.1.2 Cation exchange resin columns

8.1.2.1 Cation exchange resin, hydrogen form. Add strongly acidic cation exchange resin, 100 - 200 mesh, to 160 mℓ of 4N HCl in a 250 mℓ Erlenmeyer flask until a wet volume equivalent to 40 mℓ has settled at the bottom. Soak for at least 3 hours with occasional stirring with a glass rod. Decant the acid, add 100 mℓ deionized water, stir and decant the liquid as soon as most of the solids have settled at the bottom. This procedure removes most of the fines. Repeat rinsing procedure several times until the rinse liquid gives neutral reaction to pH paper. Transfer half of the resin to a 150 mℓ Erlenmeyer flask for conversion to the silver form.

Connect two sections of 1/4" O.D., 4 mm I.D. stainless steel tubing as in 8.1.1 with a = 9 and b = 5. The reducer on the outlet end of A should have a 5 micron stainless steel filter frit. These frits are available commercially. The frit must be able to withstand high pressure (1200 psi). (If the cation exchange resin breaks through the frit and comes to contact with the barium chloranilate column, the column gets plugged.) Connect a small funnel to open end of B with a flexible tubing sleeve. Clamp composite column vertically and connect open end of A to vacuum line equipped with liquid trap.

Fill funnel with deionized water and turn vacuum slowly so that the column is completely filled with water. Add enough water so that water level is in the funnel cone; stop the vacuum and add the slurry of freshly washed resin (H^+ form). Let the resin settle by gravity until the resin top is halfway in the funnel stem. Open the vacuum slowly and keep adding the resin slurry until the composite column is completely filled. Proceed as in 8.1.1 beginning with the sentence "Remove funnel and cap open end of B ...".

8.1.2.2 Cation exchange resin, silver form. Add 60 mℓ of 1N $AgNO_3$ solution to the other half of the washed cation exchange resin, hydrogen form, in a 150 mℓ Erlenmeyer flask. Stir with a glass rod, cover the flask with aluminum foil and soak the resin overnight.

Decant the $AgNO_3$ solution into a waste reservoir. Add 100 mℓ deionized water, stir and decant the liquid as soon as most of the resins have settled at the bottom. Repeat the rinsing procedure until the rinse liquid remains clear when treated with a few drops of 4N HCl.

Connect two sections of 1/4" O.D., 4 mm I.D. stainless steel tubing as in 8.1.1 with a = 6" and b = 5". Load the column following the procedure described in section 8.1.2.1.

8.2 Priming System for Analytical Run

Connect outlet end of cation exchange resin (Ag^+ form) column to inlet end of cation exchange resin (H^+ form) column with a low dead volume 1/16" to 1/16" stainless steel tubing connector. Similarly connect the outlet end of the second column to the barium chloranilate column. Plumb the composite column to the automated set up as shown in Figure 3. Fill solvent reservoir LR with 60% IPA, activate the HPLC pump, detector, recorder, sample injection valve, sampler and peristaltic pump. During this initial operation dip the sampling probe in 100 mℓ of 60% IPA. Set the liquid flow rate at 3 mℓ/min. (Flow rate is conveniently measured by directing the effluent from the UV detector to a microburette and measuring the time in seconds needed to fill a volume of 3 mℓ.) Let run for at least 30 minutes. Deactivate sample injection valve, sampler and peristaltic pump. Leave other components in operating mode. When absorbance background is stable at the appropriate sensitivity setting of the detector, the system is ready to analyze sulfate samples.

8.3 Preparation of Standards

Sulfuric acid, sodium sulfate or ammonium sulfate may be used as standards. Ammonium sulfate is preferred.

8.3.1 $SO_4^=$ (100 μgs/mℓ) standard, alcoholic stock solution. Dissolve 275000 ± 100 μgs of primary standard ammonium sulfate in 200 mℓ of deionized water in a 2000 mℓ volumetric flask. Add 300 mℓ pure IPA, shake vigorously until thoroughly mixed, and make up to volume with 60% IPA. Store in clean polypropylene bottles. (Note: a. There is a volume decrease of about 2.7% when two parts of water is mixed with 3 parts of IPA. b. Do not use detergents nor dichromate-sulfuric acid solution for cleaning glasswares. Sulfate background from these sources are difficult to remove. 50% (v/v) nitric acid/water is preferable.) Prepare from this stock solution $SO_4^=$ calibration standards (0.5 to 20 μgs/mℓ) by dilution of appropriate aliquots with 60% IPA. Store standards in capped polypropylene bottles.

8.3.2 $SO_4^=$ (100 μgs/mℓ) standard, aqueous stock solution. Dissolve 275000 ± 100 μgs of primary standard ammonium sulfate in 200 mℓ of deionized water in a 2000 mℓ volumetric flask and make up to volume with deionized water. Store in polypropylene bottle.

8.3.3 Alternative method of preparing calibration standards. Use a repetitive dispenser, burette or automatic syringe pump. Using either the alcoholic or aqueous $SO_4^=$ (100 μgs/mℓ) stock solution dispense appropriate volumes containing 10, 20, 40 ..., 180, 200 μgs of $SO_4^=$ into 30 or 60 mℓ polypropylene bottles. Prepare 10 for each sulfate level. Evaporate the liquids completely by placing the bottles uncapped in an oven maintained at 80 - 100°C. Cool, cap the bottles and store until ready to use. These solid standards can then be extracted in the same manner as the filter samples.

8.4 Ammonia Treatment of Filter Samples

This treatment converts sulfuric acid particulate into ammonium sulfate. Conversion to ammonium salt was observed to improve precision of sulfate measurement. Sample losses from accidental contact of the filter surface with another surface is minimized. An additional advantage is that the sulfate is converted to the same form as the calibration standard.

Figure 5 shows a simple schematic of an ammoniation set-up. Filter samples on open Petri dishes are placed face up on perforated shelves of the ammoniation box. The box is evacuated, valve V_1 is closed, and valve V_2 is opened. Ammonia from concentrated ammonium hydroxide fills the box and converts sulfuric acid to ammonium sulfate. One hour exposure to ammonia vapor is adequate. V_2 is closed, most of the ammonia is pumped out and passed through a KH_2PO_4 scrubber column. Vacuum is released by switching V_1 to vent.

8.5 Extraction of Soluble Sulfates.

It is important that the water/IPA ratio in the sample and in the mobile phase be the same. A sample richer in water content than the mobile phase will momentarily increase the solubility of barium chloranilate and will produce a positive peak above a flat background; that richer in IPA will produce a negative peak. Variations will occur if the solvent used in the preparation of the standards and in the extraction of the filter samples were taken from a different stock as that used in the mobile phase. Therefore, it is strongly recommended that the extraction solvent be taken from the same stock solution as the mobile phase or, if possible, directly from the liquid reservoir of the HPLC pump. The use of solid standards as prepared in 8.3.3 will eliminate variability due to IPA/water mismatch.

8.5.1 From fluorocarbon membrane filters

Place filter in appropriate size polypropylene bottle. If approximate sulfate level is known from previous analysis of similar samples, measure adequate volume of 60% IPA to give sulfate concentration of about 10 μgs/mℓ. Otherwise add 10 mℓ 60% IPA and cap the bottle tightly. As a rule of thumb, the sulfates constitute about 40 - 50% of the total particulate mass if most of the particulates on the filter is sulfuric acid. Such cases are generally encountered with filter samples from catalyst equipped cars run on non-leaded fuels. Particulate mass loading of a filter is an important piece of information in deciding appropriate volumes of extracting solution to use.

Shake the bottle vigorously until the filter collapses and is completely immersed in the solvent. A vortex test tube mixer is recommended. Twenty seconds shaking with a vortex test tube mixer is adequate to leach the soluble sulfates from the filter. If there are no visible suspended particulates, the clear solution can be used directly for analysis. If suspended carbon or other particles are apparent, filter about 5 mℓ of the extract by using a syringe with a μ pore size fluorocarbon in-line filter. These filter syringes are available commercially. If the particles are sufficiently large, they can be removed from the bulk solution by centrifugation.

8.5.2 From glass fiber filters.

This procedure is for the extraction of 47 mm diameter filters. Adjust the volume of the extracting solvent accordingly for different size filters.

Place the filter in appropriate size polypropylene bottle. If approximate $SO_4^=$ level is known, add adequate volume of 60% IPA to give sulfate concentration of about 10 μgs/mℓ. Otherwise, add 30 m 60% IPA and cap bottle tightly. Shake with a vortex mixer until the glass fibers disintegrate. Where large solvent volume and inordinately long shaking time are required, stirring with a Teflon clad magnetic stirring bar is preferable. Glass fibers are easily separated from the bulk liquid by using a centrifuge. If finely suspended particles are present, as in the case of diesel and some non-catalyst exhaust samples, syringe filtration as mentioned in 8.5.1 must be used. In some cases a 0.2 μ pore size filter is necessary.

8.6 Water extracts.

Water extracts of filter samples may also be analyzed by the automated BCA method. One important requirement, however, is that the solution must be made up to 60% IPA (e.g., 4 parts of the extract must be added to 6 parts of pure IPA, v/v) before the sample can be analyzed. If the water extract is mixed directly with pure IPA, volume shrinkage (about 2.7%) must be taken into account in the calculation of concentrations.

Another approach is to evaporate completely the solvent in a known volume of the extract in polypropylene bottle similar to the preparation of solid calibration standard in 8.3.3. The residue may be ammoniated in the plastic bottle as in 8.4 and extracted as in 8.5.1 or 8.5.2.

8.7 Analysis

Set instrument in operating mode, remove sample probe from the holder and dip in 100 mℓ 60% IPA. Adjust the flow rate at 3 mℓ/min., allow the instrument to cycle several times until a stable background is obtained, then remount sample probe to holder. Adjust loading time or peristaltic pump rate so that at least twice the volume of the sample as the volume of the sample injection loop has exited the waste port of the sample injection valve. Adjust sample injection time so that peaks from successive sample injections do not overlap. Fill sample cuvettes with samples and rinse solution (60% IPA) and place according to a sampling pattern, blank, sample, blank, sample, blank... The rinse solution (blank) is necessary to ascertain that there is no memory effect from previous sample injection.

A series of at least 6 calibration standards spanning the concentration range of interest is run before samples are run. A control standard may be placed every 10 samples as a quality check on the stability of the system. Dilution may be necessary if the sample peak height is beyond the range of the calibration standard. If a large number of samples needs dilution, it may be more convenient to merely change the size of the sample loop.

Plot peak height (or area if an integrator is also used) vs concentration in μgs/mℓ of the sulfate standard. The curve is not linear. Alternatively, the peak height or area concentration data may be fitted into a polynomial of the form:

$$y = a_o + a_1x + a_2x^2 + a_3x^3 + a_4x^4 + \ldots$$

where: y = sulfate concentration in μgs/mℓ

x = peak height or area

8.8 Calculations

Calculate the concentration of sulfate as μgs $SO_4^=$/mℓ using the calibration curve or the polynomial regression equation. Total soluble sulfate $(SO_4^=)_F$ in the filter is then given by:

$$(SO_4^=)_F = (SO_4^=)_d \times V_o \times d$$

where: V_o = total volume in mℓ of original sample extract

$(SO_4^=)_d$ = sulfate concentration of the diluted sample in μgs/mℓ

d = dilution factor

= 1, if there is no dilution of the extract before analysis

= V_a/V_d

V_a = aliquot volume in mℓ of sample diluted with 60% IPA

V_d = final volume in mℓ of the aliquot sample after dilution with 60% IPA

Example:

Suppose 10 mℓ of 60% IPA was used to extract the soluble sulfates in the filter and that 2 mℓ of this was further diluted with 4 mℓ 60% IPA to bring detector response within calibration range. Suppose that the concentration of the diluted sample was found to be 5 μgs/mℓ. Then,

$(SO_4^=)_d$ = 5 μgs/mℓ

V_o = 10 mℓ

V_a = 2 mℓ

V_d = 2 + 4

= 6 mℓ

$(SO_4^=)_t$ = 5 x 10 x (6/2)

= 150 μgs

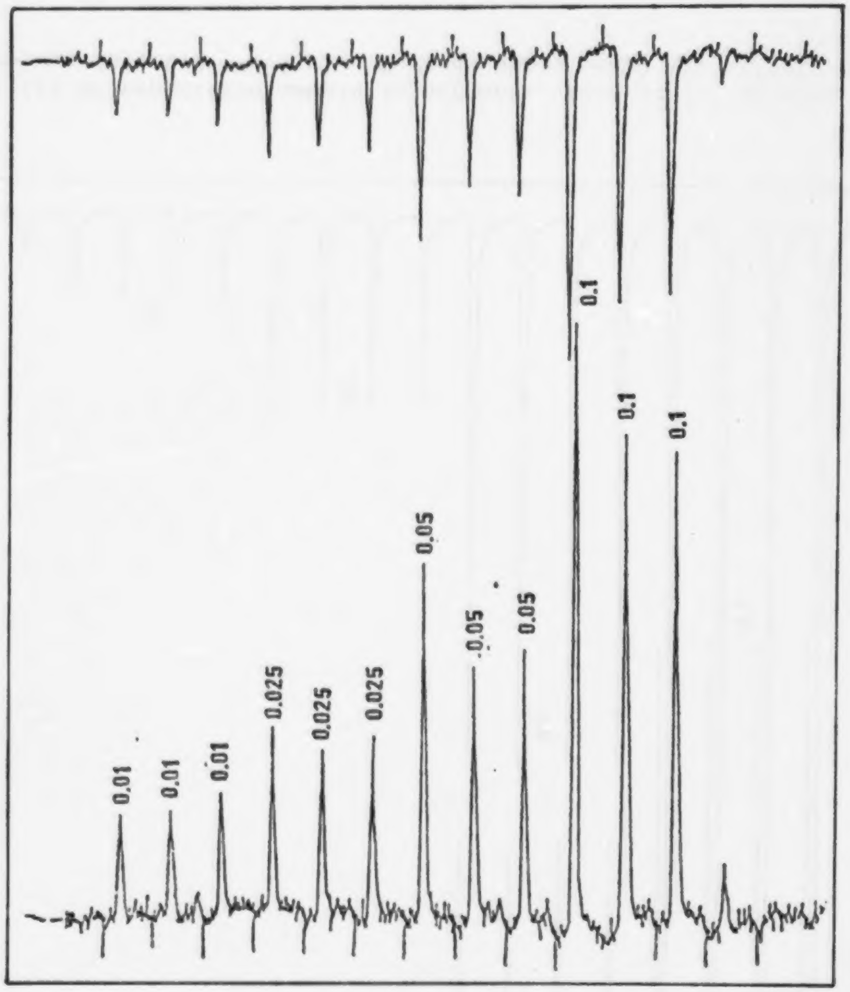


Figure 1. Chromatogram at trace sulfate levels, 0.01, 0.02, 0.05, 0.01 µgs $SO_4^{=}$/ml. Flow rate at 3.2 ml/min. Detector sensitivity at 0.01 absorbance units full scale. Sample volume injected = 0.5 ml.

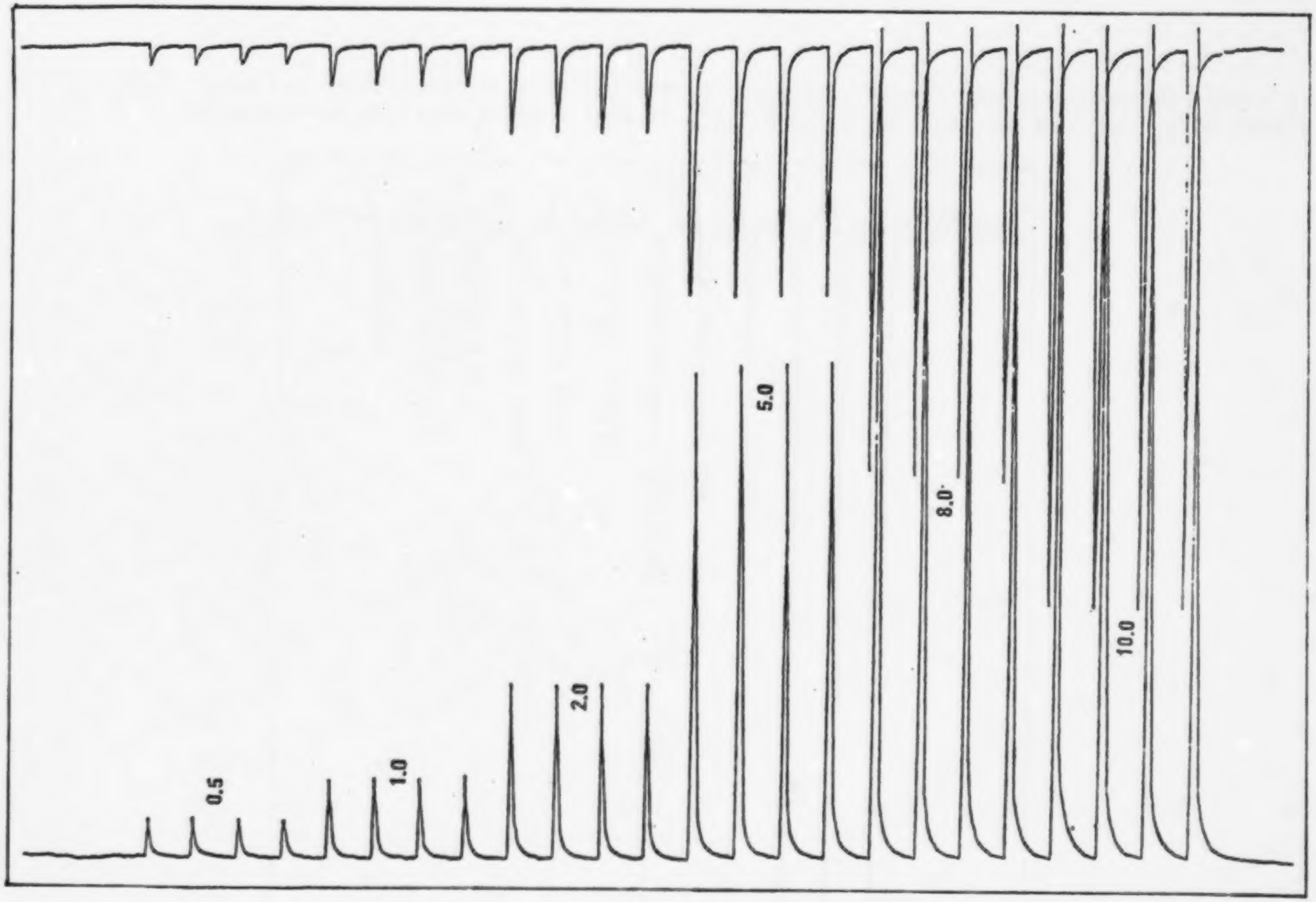
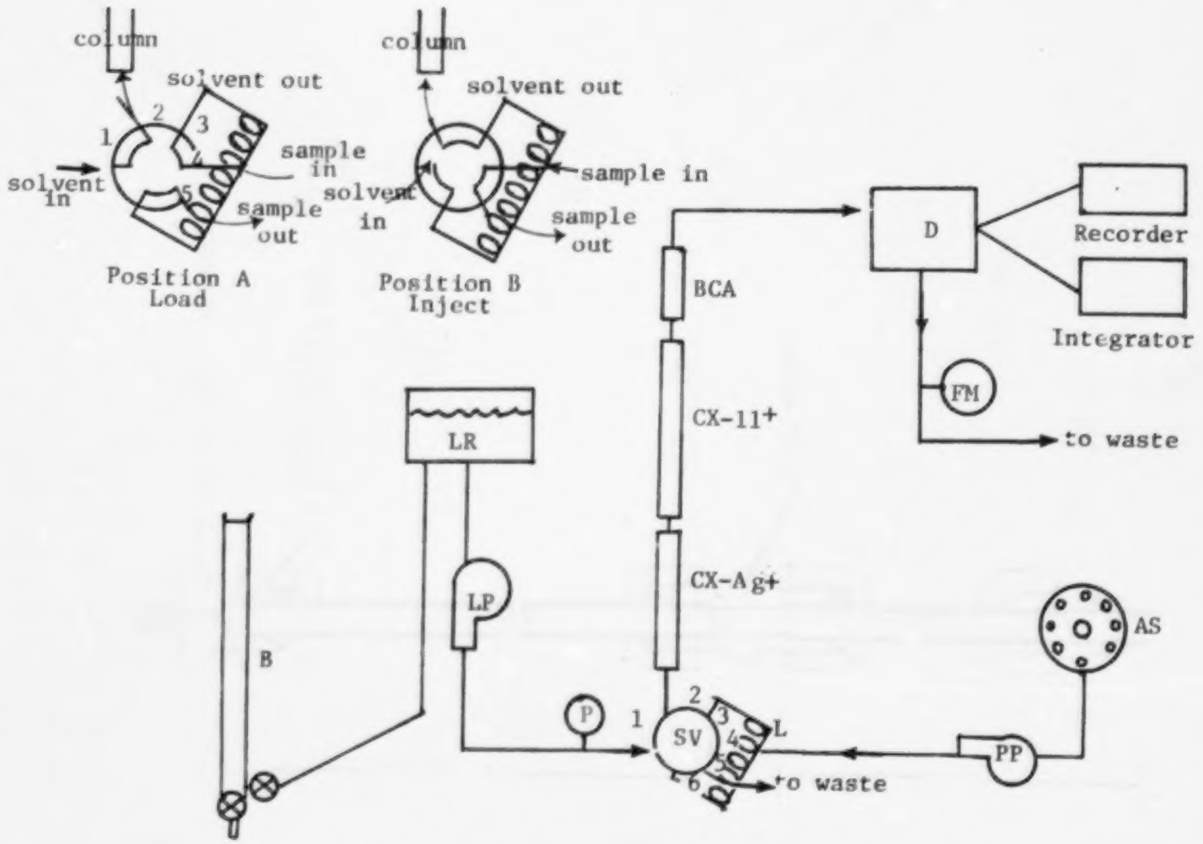


Figure 2. Reproducitility of repetitive sample injections. Flow at 3.2 ml/min. Detector sensitivity at 0.5 AUFS. Sample volume injected = 0.5 ml. Numbers above peaks are sulfate concentrations in μgs/ml.



column
solvent out
1
2
3
4
5
sample in
solvent in
sample out
Position A
Load
column
solvent out
sample in
solvent in
sample out
Position B
Inject
D
Recorder
Integrator
BCA
FM
CX-11+
to waste
LR
CX-Ag+
LP
AS
B
P
1
2
3
4
5
6
SV
L
PP
to waste

B - buret
LR - liquid reservoir
LP - PHLC pump
P - Pressure Monitor
SV - Sample Injection valve
L - Sample loop

CX-Ag+ - Cation exchange resin, silver form
CX-H+ - Cation exchange resin, hydrogen form
BCA - Barium chloranilate
D - UV detector
FM - Flow monitor
PP - Peristaltic pump
AS - Automated sampler

Figure 3. Schematic of an automated BCA sulfate set-up.

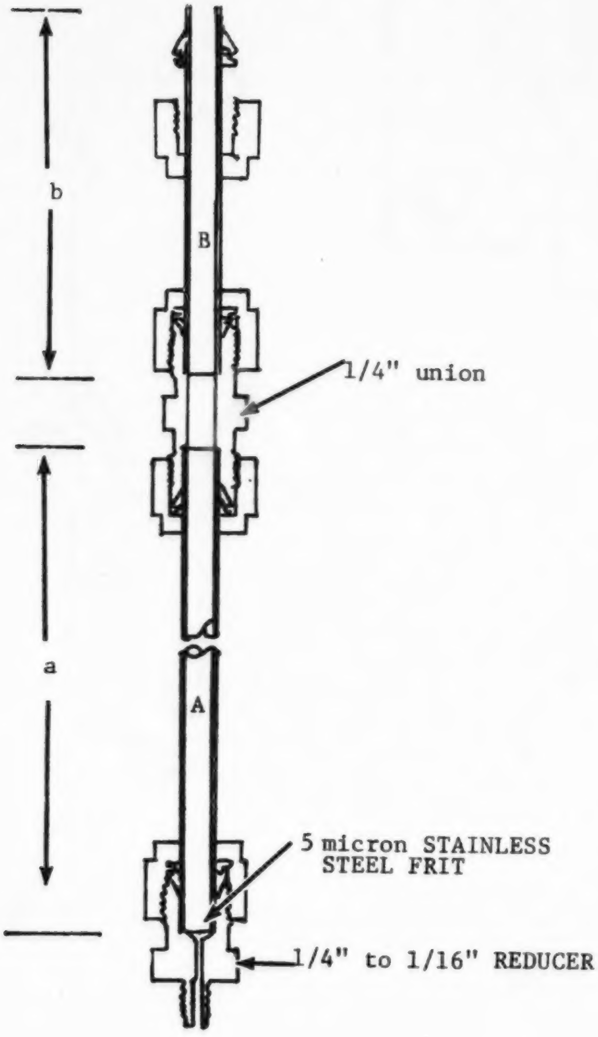

b
B
1/4" union
a
A
5 micron STAINLESS STEEL FRIT
1/4" to 1/16" REDUCER

Figure 4. Configuration for packing column.

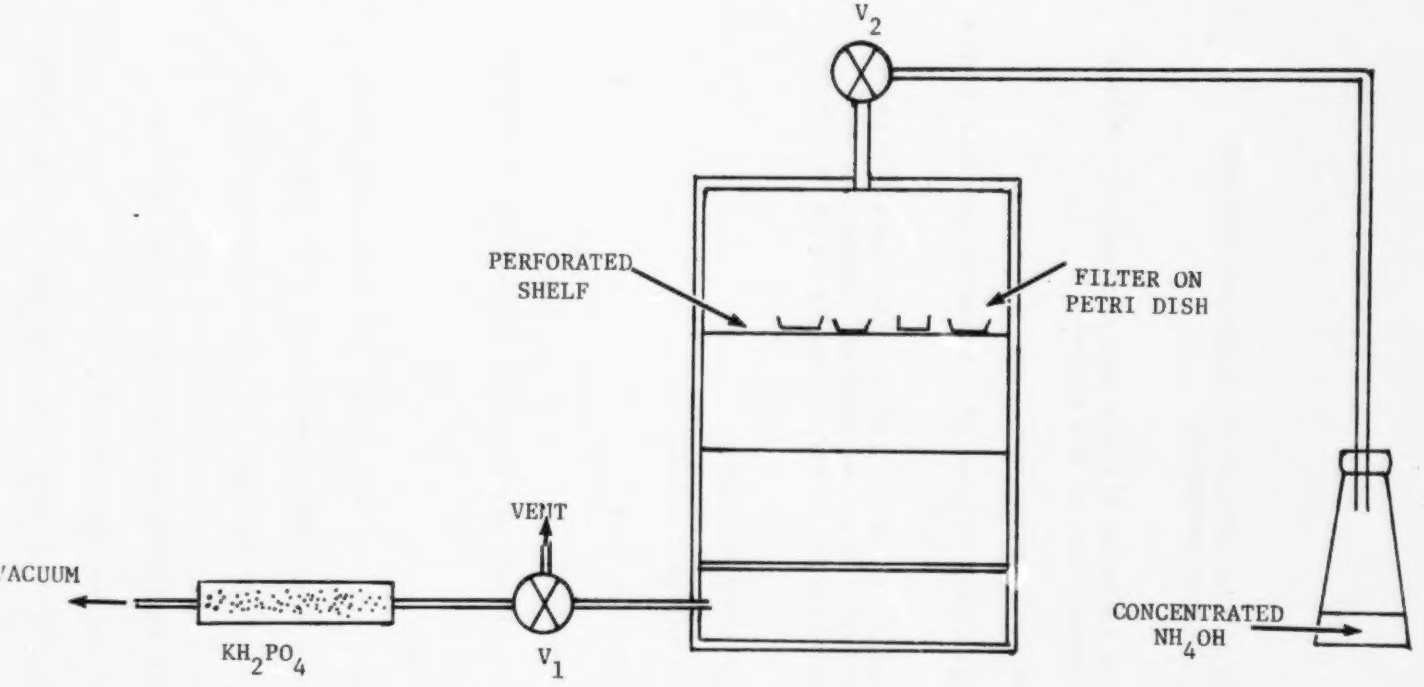

V$_2$
PERFORATED SHELF
FILTER ON PETRI DISH
VENT
VACUUM
KH$_2$PO$_4$
V$_1$
CONCENTRATED NH$_4$OH

Figure 5. Schematic of an ammoniation set-up.

DISCREPANCIES BETWEEN EPA AND DEPARTMENT OF EMISSIONS RESEARCH BCA SULFATE PROCEDURE

4.1.1.1 - Bottled N_2 gas is used to drive 60% IPA from a reservoir through the HPLC system at average rate of 4.5 mℓ/min.

4.1.1.2 - The Dupont 837 sample cell volume is 6.3 μℓ.

4.1.1.3 - A dedicated 1 mℓ sample loop is used on a manually-operated sample injection valve.

4.1.1.4 - Recorder is dual channel, 10 mv full scale, with variable chart speed set at 0.75 in./min. Only one recorder channel is used since chromatogram sensitivity is controlled at range switch on spectrophotometer.

4.1.1.6 - A 6-inch long cation column is used.

4.1.1.7 - A 2-1/2 inch long BCA column is used.

4.1.1.10 - One-quarter inch unions are used.

4.1.2 - Non-automated system is used.

6.5 - Polypropylene bottles (30 mℓ) are used for extraction of filters in 60% IPA solution.

6.8 - We don't use centrifuge.

7.2 - We use deionized water checked with $AgNO_3$ for dissolved salts.

7.3 - We store in a 5-gallon stoppered glass bottle with dispenser.

7.7 - Ours is ACS reagent, oven dried, and stored over silica gel in a dessicator.

8.3.1 - Stock and calibration standards are stored in glass bottles.

8.3.2 - Standard solution stored in glass bottles.

8.3.3 - We don't use alternative method of preparing calibration standards.

8.4 - The chamber containing sample filters in open Petri dishes is purged with ammonia from concentrated ammonium hydroxide which is then vented out via hood. The chamber is purged for 3 minutes and then the filters are isolated in the ammonia-filled chamber for one hour before their extraction in 60% IPA.

8.5.2 - We do not use glass filters for sulfate analysis.

8.6 - We do not do water extracts.

8.7 Used in automated system only.

APPENDIX M

DMNA SAMPLING PROCEDURE

DESIGN AND CALIBRATION OF SECONDARY DILUTER

A secondary diluter, to be used in conjunction with a constant volume sampler, has been constructed. The secondary diluter was constructed:

1. to determine the concentration of N-nitrosodimethylamine in automobile exhaust
2. to determine the composition of condensable organic vapors in automobile exhaust. Condensable organic vapors are those having molecular weights from about 140 to 300 atomic mass units.

Factors which had to be taken into consideration for construction of the secondary diluter were:

1. a proportional sample of automobile exhaust is needed
2. high levels of nitric oxide must be avoided because:
    a. NO + amine → nitrosamine artifact, which would interfere with the detection of N-nitrosodimethylamine.
    b. the oxidation of NO to NO_2 with materials in the system and on the traps would cause interference.
3. the sample must be presented to the Tenax G.C. trap at an appropriate flow rate and temperature so that collection is efficient and materials are not driven off the trap. (We sample at 1.6 ℓ/min and 60°C.)

The design criterion was to avoid oxidation of NO_x and have a sample of 5 ppm or less of NO_x, which was accomplished by using dry nitrogen to dilute the automobile exhaust at 25:1. (Our dilution is 16.7:1.)

The secondary diluter is shown schematically in Figure 1 and its operating principles given below:

1. diluted automobile exhaust is pulled into the secondary diluter through a 1/8" O.D. stainless steel tube at a flow rate of approximately 2.5 ℓ/min; this flow is dependent upon the downstream pressure drop.
2. Dry nitrogen for secondary dilution is added through a roots meter and rotometer, in series, at approximately 68 ℓ/min. This flow is independent of the downstream pressure drop. (We run at 55 ℓ/min.)

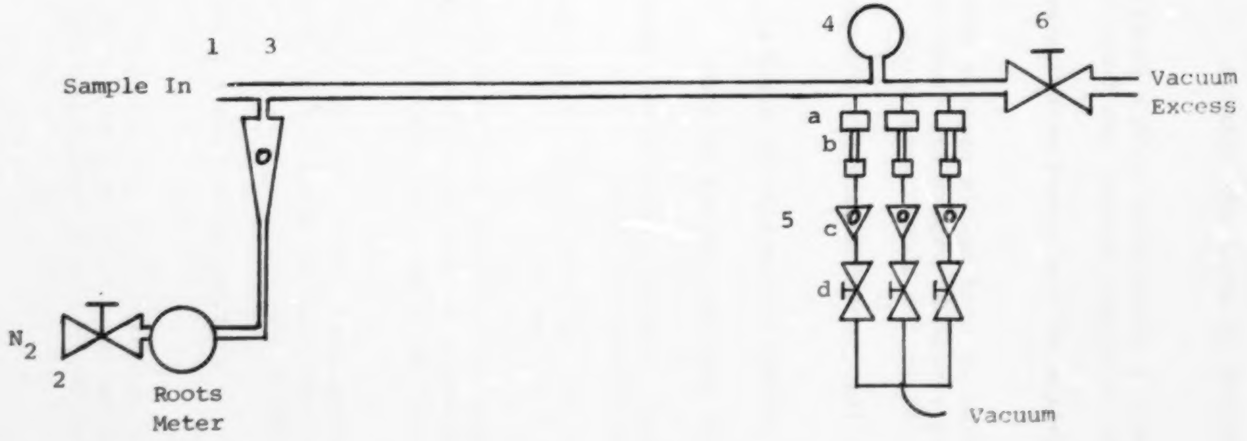

1
3
Sample In
4
6
Vacuum
Excess
a
b
5
c
d
Vacuum
N$_2$
2
Roots
Meter

Figure 1. Secondary diluter.

3. Diluted automobile exhaust and dry nitrogen are mixed at this point and pulled through a 3/8" O.D. stainless steel tube 13" long.

4. A magnehelic gauge is used to monitor the pressure drop across the diluter. The reference side of the magnehelic is connected to the primary dilution tube; this allows dilution ratios to be determined without making corrections for differences in atmospheric and primary dilution tube pressure.

5. Three simultaneous samples are pulled through; (a) glass fiber filters, (b) Tenax G.C. traps, (c) rotometers, and (d) needle valves. The needle valves are set to maintain a flow of 2.5 ℓ/min through each sample trap. (We use Fluoropore filters and sample at 1.6 ℓ/min.)

6. Excess flow is discharged from the diluter through a needle valve, which is used to maintain the proper pressure drop across the diluter.

During the operation, it is suggested that the inlet rotometer (2) be maintained at 80 and the magnehelic gauge, (4) be maintained at 10" water, which will give dilution ratio of 25:1. These gauges should be checked every five minutes to be sure that these flows do not change. (Our rotometer is set at 65 and the magnehelic at 25" water for a dilution ratio of 16.7:1.)

CALIBRATION

The rotometers for the secondary diluter were calibrated by using a roots meter and dry test meter.

The secondary diluter was calibrated by several different, but similar experiments. The purpose of these experiments was to calibrate the dilution ratio against diluter pressure drop. Each experiment involved measuring dilution ratios obtained at various constant diluter, pressure drops as measured by the magnehelic gauge.

It was found early in the experiments that a constant source of vacuum is needed in order to maintain a steady pressure drop across the diluter.

The experiments were conducted as follows:

1. A sample of propane span gas was placed in a large empty Tedlar bag; the concentration of propane in the bag was determined by analyzing the contents of the bag on a hydrocarbon analyzer.

   One sample rotometer (5) was disconnected from its normal vacuum source and replaced by a diaphram pump of sufficient size to pull 2.5 ℓ/min. The reference side of the magnehelic was left open to atmospheric pressure, a correction for this was made for this calculating the data. The rest of the system was up as it would be for normal operation. The bag of propane span gas was connected to the sample inlet (2). The diluted sample was then collected in an empty Tedlar bag downstream of the diaphragm pump. This bag was then analyzed on a hydrocarbon analyzer and its concentration determined. By dividing the concentration of hydrocarbon in the span gas by the concentration found in the bag of diluted span gas, the dilution ratios were found for different magnehelic gauge readings.

2. The diluter was then set up as it normally will be used, except that one rotometer (5) was still connected to the diaphragm pump. A cylinder of span gas containing propane, carbon monoxide and carbon dioxide was then metered into the primary dilution tube. A sample of this diluter span gas was collected in bags on the primary diluter and at the same time bags were collected on the secondary diluter. The bags collected on both primary and secondary diluters were then analyzed on appropriate analyzers. By dividing the concentration found in the primary bag by the concentration found in the bag of diluted span gas, the dilution ratios were found for different magnehelic gauge readings.

3. The diluter was set up as it would be for making a normal test, with the exception that a rotometer was attached to the sample inlet (1). Ambient air was pulled through this rotometer while the rest of the diluter was under normal operation. By making corrections for pressure drop in the diluter, the flow of dry nitrogen into the diluter can be divided by the flow of ambient air into the diluter, giving dilution ratios for different magnehelic gauge readings. The expression used for correcting the pressure drop is $\frac{P_1V_1}{P_2} = V_2$ where:

   P_1 = initial pressure
   V_1 = initial volume
   P_2 = final pressure
   V_2 = final volume

A correction for temperature was not made because the temperature was stable at approximately 20°C and thought this difference would be of little consequence.

The dilution ratios determined by these three different experiments were plotted against differential pressures measured by the magnehelic gauge using the general expression for flow in pipes:

$$AP = \frac{2\ f'l}{VGD} V_2 \text{ (ref. 1)}$$

where: AP = differential pressure
f' = friction
L/D = length/diameter ratio
g = gravitational constant
v = specific volume of gas, 1/density
V = linear velocity

Since the sample inlet is of constant cross section, the linear velocity is proportional to the volumetric flow rate. In any given set of experiments, all variables in this equation other than velocity and pressure are constant. Because of this, the equation reduces to:

$$\Delta P = CV^2 = CQ^2$$

where $Q = \frac{\text{sample flow rate}}{\text{volumetric}}$

The dilution ratio, R, is given by:

$$R = \frac{Q_{N2} + Q_s}{Q_s}$$

If $Q_s \sim Q_{N2}$, then $R = \frac{Q_{N2}}{Q_s}$; $Q_s = \frac{Q_{N2}}{R} = \frac{\text{Constant}}{R}$

Therefore: $\frac{1}{R} = C'' \sqrt{\Delta P}$

and the plot of the reciprocal of the dilution ratio against $\sqrt{\Delta P}$ should be a straight line.

Figure 2 presents all the raw data gathered in these calibrations and plotted on this basis. A linear least squares fit for these data is also presented in Figure 2. A single equation was found to adequately represent the shole date base:

$$1/R = 0.01858 \sqrt{\Delta P} \ 0.02133$$

$$r^2 = 0.9819$$

standard error of estimate = 3 percent of mean value

Reference 1: Mark's Standard Handbook for Mechanical Engineers, 7th Edition, McGraw-Hill, N.Y. (1967), p. 4-66.

PROCEDURE USED BY SWRI FOR OBTAINING DMNA TRAPS

PREPARATION FOR RUNNING

1. Turn on 4 rheostats in back of DMNA cart at least 30 minutes prior to test.

2. Remove trap holder with the filter case from the cart. Insert filter (FA) into filter case so that flow goes through the dull side of the filter (note direction of arrow). Replace o-ring. The filter and the o-ring are not to be handled with bare hands. Fasten trap holder back onto cart and tighten nut.

3. Check nitrogen (N_2) bottle to make sure it has at least 1000 psi. If necessary, N_2 flow can be set with a dummy filterwith the pump on. Check dryer on N_2 bottle and replace molecular sieve and silica gel dryer if necessary.

4. Open the green valve on the sample line.

READY TO RUN

1. Obtain trap from refrigerator. Leave it in the glass tube until ready to use. With disposable gloves, place trap in holder. Hand tighten both end fittings. Replace spun glass ball in glass container and recap.

2. Just prior to start of test, turn on N_2 flow. At honk of horn, turn on sample pump and set the large N_2 flowmeter with the top of the float at 65 and the magnehelic at 25" H_2O. Both knobs need to be adjusted simultaneously since they are dependent on each other. These two will have to be monitored throughout the test. Flowmeters 1, 2, and 3 should already be adjusted to their proper settings (10, 5.2, 10 respectively). If not, use the large black knobs to readjust. Temperature of the system is monitored at four points: sample inlet from CVS, N_2 inlet, mixing point and at trap. It should be set at 60°C (140°F) by adjusting rheostats in back of cart. These temperatures are recorded on the data sheet about once a week.

END OF TEST

The traps are run the full cold FTP and then the hot 505. During the soak between FTP's, the pump and the N_2 bottle are shut off.

1. When the test is over, the trap is again carefully handled with gloves and placed back in the glass container. The container is labeled on the cap and on the side with the trap number (from log book), test number and run date. The container is then placed in the 1-gallon can in the refrigerator. Test number and run date are recorded in the log book. Test number is also recorded on the data sheet (same one temperatures were recorded on).
2. Close green flow valve on sample line.
3. Turn off N_2 regulator.
4. Turn rheostats off.

TABLE 1. N_2 SECONDARY DILUTER CALIBRATION VALUES
FEBRUARY 10, 1976

	1/DF		
$\sqrt{\Delta P}$	Carbon Monoxide	Propane	Rotameter
2.0	0.01712		
2.236	-------	0.01908	0.02116
2.5495	0.02500	-------	-------
2.7386	-------	-------	0.03001
2.8284	-------	0.03175	-------
3.1623	0.03650	-------	0.03882
3.3166	-------	0.03937	-------
3.5355	-------	-------	0.04062
3.7417	0.04651	0.05110	-------
3.87298	-------	-------	0.05013
4.12311	-------	0.05701	-------

	$1/DF = A (\sqrt{\Delta P}) + B$			Overall Data
A	0.01709	0.02030	0.01684	0.01858
B	-0.01765	-0.02630	-0.01622	-0.02133
R^2	0.99749	0.99414	0.97560	0.0818
(2)	0.01653	0.01430	0.01747	0.01584
(4)	0.05071	0.05491	0.05115	0.05301